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TRANSACTIONS OF THE AMERICAN • SOCIETY • FOR METALS

MARCH, 1938

lume XXVI Number 1

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The TRANSACTIONS *of the*
AMERICAN SOCIETY FOR METALS

Published quarterly and Copyrighted, 1938, by the AMERICAN SOCIETY FOR METALS
7016 Euclid Avenue, Cleveland, Ohio

SUBSCRIPTIONS: (members) $2.50 per year
(non-members) $5.00 per year, $2.00 per copy
Foreign (non-members) $6.50 per year, $2.50 per copy

Entered as second class matter, November 9, 1931, at the Post Office at Cleveland, Ohio, under the Act of March 3, 1879

RAY T. BAYLESS, *Editor*

Vol. XXVI March, 1938 No. 1

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TRANSACTIONS
American Society for Metals
VOL. XXVI JANUARY-DECEMBER 1938

QUANTITATIVE HARDENABILITY

By J. L. Burns, T. L. Moore, and R. S. Archer

Abstract

Standardization is proposed with respect to a test for hardenability, and a method of expressing results in quantitative but simple terms. Details of testing procedure are described. Reproducibility of results is found to be considerably better than required. The test is considered practical for regular use where close control of hardenability is economically justified.

The maximum hardness attainable on quenching is shown to depend on carbon content alone, in the case of plain carbon and common alloy steels.

Penetration effect depends chiefly on chemistry and austenite grain size. The effects of these factors on hardenability are indicated in a quantitative manner for a wide range of plain carbon steels. Relationships between mass and penetration are illustrated with respect to three steels quenched in sections from ¾ to 3 inch diameter.

THE ability of steel to harden on quenching has assumed increasing importance as industry has expanded and progressed. The ancients knew how to make steel or carburized iron which would harden sufficiently for their weapons and simple tools. The carburizing of wrought iron bars to make "blister steel" was practiced in the middle ages. It remained for Nineteenth Century chemistry to develop methods for determining carbon content so that the effect of this element on hardening power could be studied quantitatively.

Introduction of the Bessemer and open-hearth processes led to

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. Of the authors, J. L. Burns and T. L. Moore are members of the Metallurgical Staff, Republic Steel Corporation, Chicago District, and R. S. Archer is Chief Metallurgist, Republic Steel Corporation, Chicago District. Manuscript received June 16, 1937.

the discovery of the value of manganese in overcoming hot-shortness. Ferromanganese was not available in this country when the first open-hearth furnace was built in 1868 and some of the next open-hearth plants to be built included crucible furnaces for the local manufacture of ferromanganese. From this it can be seen that knowledge of the effect of manganese on hardening characteristics must be recent.

Toward the close of the last century the armament industry in particular brought out the effects of certain other alloys, such as nickel and chromium, on depth of hardening. It remained for modern mass production, notably in the automotive industry, to bring out the influence of deoxidation practice as indicated by austenitic grain size (1), (2).[1]

We may consider that the principal factors now known to affect the ability of steel to harden on quenching are (a) carbon content, (b) content of certain alloy elements other than carbon, and (c) "grain size." These factors were discovered in the order of their importance. This suggests that any additional factors which may be discovered are apt to be less important than those already known.

Within the last few years the term "hardenability" has come into rather common use, but without a very definite meaning. Its general significance seems to include two distinct characteristics: (a) maximum attainable hardness on quenching, and (b) penetration, or depth of hardening. The first of these can be expressed simply and quantitatively by hardness values in accordance with any of the recognized methods of testing. The penetration factor is indicated by various tests, some of which have been used for many years, but in this country there is no widely used standard test and hence no generally accepted measure of the penetration effect.

Fundamental properties which might be considered in this connection are the "critical cooling velocity" and the "austenite transformation rate," at some specified temperature. Unfortunately, it is tedious to determine these values experimentally, and is still more of a problem to employ them in practical heat treating problems.

In selecting a type of steel for a given application involving heat treatment, or in judging the suitability of a particular heat of steel for such a purpose, it is now common practice to appraise probable hardenability on the basis of chemical analysis and "grain size," usually as determined by the standard McQuaid-Ehn test. Assuming that some definite range of hardenability is the chief requirement, we

[1]The figures appearing in parentheses pertain to the references appended to this paper.

are using these indirect measures or indicators of this property where it would seem that we might better use a direct test for hardenability.

With this thought in mind, the authors have sought to select or develop a hardenability test suitable for a wide range of commercial applications. Such a test must meet the following requirements:

(1) The results must be sufficiently indicative of the behavior of the steel in heat treatment.
(2) Results on duplicate specimens by different operators must be reproducible within limits of error which are not significant in practical heat treatment.
(3) The test must be reasonably economical.
(4) The test must be reasonably rapid.
(5) Results should be so expressed that they can be easily transmitted by telephone or telegraph.

After considering several methods of testing and doing some preliminary work, the authors concluded that these requirements could be met to a useful degree by further development of a test

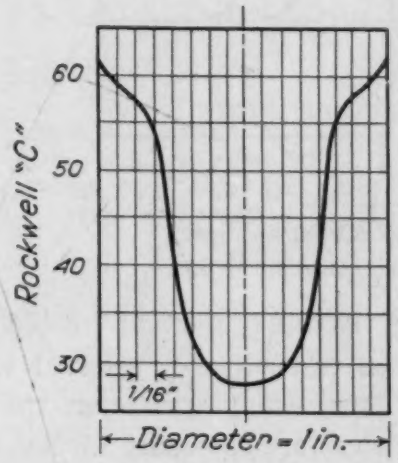

Fig. 1—Typical Hardenability Curve Where Hardness is Plotted Against the Diameter of a Round Quenched Specimen as Suggested by Bain (3).

which has already been employed by several investigators, mostly for research purposes (3). This is the test in which a round bar is hardened, and the hardness from surface to center is measured on a cross section cut about half way between the ends of the specimen. It has been common to represent results in the form of a curve in which hardness is plotted vertically and the diameter of the specimen horizontally. (See Fig. 1).

From curves of this type, differences in actual hardness or in hardness penetration can be recognized at a glance, especially by

superimposing one curve upon another plotted to the same scale. Published curves have been used, almost without exception, to illustrate in a *qualitative* manner differences in hardenability due to grain size, composition, quenching method, or the like. Curves published by different investigators can not easily be compared unless they are plotted to exactly the same scale.

To obtain numerical measures of the penetration effect for more ready comparisons, there has been some use of areas bounded by

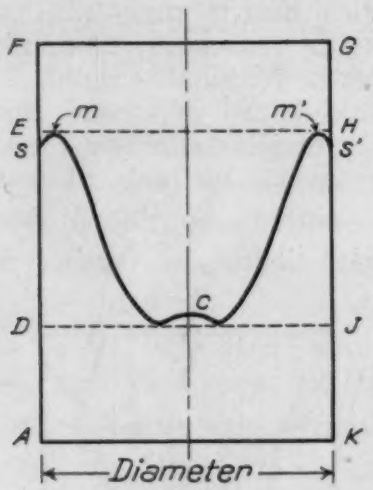

Fig. 2—Hardenability Curve with Special Features.

hardenability curves. A common method of obtaining such areas has been to plot the curves to arbitrarily selected scales and measure the desired area with a planimeter, or estimate the area by counting enclosed squares. Such areas are in square inches, and have no fixed relationship to hardenability except with respect to the particular scales which have been chosen.

Let us refer to Fig. 2 for more specific consideration.

s — surface hardness
m — maximum hardness
c — center or core hardness

The curve of Fig. 2 intentionally shows two peculiarities which are, in the authors' experience, sometimes but not usually observed:

1—Maximum hardness occurs below the surface, but is only slightly above surface hardness. In steels of the 1045 type, this is more apt to be found with coarse grain than with fine grain. It may be due to austenite retention at the surface, to lower carbon content

at the surface resulting from ingot segregation (assuming that precautions have been taken to avoid decarburization in heat treatment), or to age-hardening of the martensite just under the surface.

2—Hardness rises slightly at the center. This is especially apt to be noted if the value taken for center hardness is that of a single hardness test taken at the exact center of the specimen. The effect is often due to positive segregation (of carbon in particular).

There is occasionally an abnormal *drop* in hardness at the center because of negative segregation.

Herty (4) has considered that the area DEHJ (Fig. 2) represents maximum potential hardening, which would seem to imply that no hardening has taken place at the center. As a matter of fact, the present investigation has shown that the hardness at the center of ordinary carbon forging steels, quenched in 1-inch rounds, is always substantially above the normalized hardness. On the basis mentioned, however, Herty further considers that the area Dscs′J represents actual hardening, from which he derives the ratio:

$$\frac{\text{Dscs′J}}{\text{DEHJ}} = \text{per cent hardened}$$

A large industrial user of steel has employed the area above the curve, sFGs′c, as a measure of the extent to which the steel has failed to harden completely. The point F is taken at 70 on the Rockwell C scale with the idea that this represents approximately the maximum hardness obtainable in any steel. The area so determined, measured in square inches on an arbitrary but consistent scale, has been used successfully in the application of steel for heat treated parts.

From this and other evidence, the authors have concluded that area measurements of some sort can be very useful. It is obvious that various areas bounded by the hardenability curve could be used, and that the vertical and horizontal scales selected for plotting the curve are immaterial, providing a consistent practice is followed.

The practical use of such area measurements is relatively new, and standard practices have not been developed so that results in different laboratories and plants can be readily compared. One of the objects of this paper is to suggest:

1—a standard area,
2—a definite and standard unit of area measurement, and
3—a simple method of determining the "area" in these units without plotting the curve.

Standard Area—The area proposed is Ascs'K, where A is taken at zero on the Rockwell C scale. This area is indicative of hardenability, and is the easiest area to determine directly from hardness data.

Unit of Area—The proposed unit is the "Rockwell-inch," which is the product of hardness in Rockwell C units by the diameter of the specimen in inches.

Measurement—Each point plotted to establish a hardenability curve represents a hardness value at a certain distance from the surface of the specimen. It is common to draw a smooth curve through or near these points. Instead, let us connect the points by short straight lines. The area under this curve is then the sum of a series of trapezoids whose mean altitudes are given by the hardness data, and whose widths are the distances between the hardness determinations from surface to center of the specimen. The desired value is obtained by a simple formula, as will be explained in detail later.

For a given grade of steel the "area" under the hardenability curve is a very useful index, but it does not represent all of the information of the actual hardenability curve. Two additional numerical values can easily be given which, together with the "area" value, describe the curve almost completely. These are the values for surface hardness and center hardness. It is, therefore, proposed that these three numerical values, namely, surface hardness, "area," and center hardness, be used to describe hardenability. For example, a specimen representing a heat of S.A.E. 1045 steel might show a surface hardness of 62, an area value of 46, and a center hardness of 30. The hardenability rating would then be expressed by the numbers 62-46-30, which could be easily transmitted by any means of communication.

It is, of course, desirable to standardize the details of testing as well as the method of expressing results. This was one of several objectives of hardenability studies made by the authors on about 120 basic open-hearth heats of special requirement carbon steel. Conclusions reached regarding details of testing are presented herewith.

Diameter of Specimen—Grossmann (5) has shown that for a given grade of steel a certain diameter of specimen is the most sensitive for measuring hardness differences in that grade. The present authors were interested principally in measuring these differences in medium (plain) carbon steels, even though the scope of this work is somewhat broader; our preliminary work indicated that a 1-inch

round was the most suitable diameter to meet this requirement, so this standard was adopted. (Also see Fig. 9).

Length—The shortest sample which could be conveniently handled, and which would not introduce variables from end-quenching effects, was considered the most suitable. After comparing results on different lengths, a 4-inch length was chosen. The results were duplicated on a 6-inch length. A shorter sample offered handling difficulties and might lead to trouble from end-quenching effect or from tongs.

Finish—The sample diameter was held within plus or minus 0.003 inch and finished on the lathe with a No. 3 emery cloth for purposes of standardization and practicability.

Source of Specimen—The specimens used in this investigation were forged from billets to 1⅛-inch round, using, in general, the entire cross section of a billet. In special cases it may be desirable to take the specimen off center. No attempt was made to control forging temperatures except for the usual precautions with respect to burning and cold forging.

Normalizing—The forged specimens were normalized in an electric furnace for one hour at 1700 degrees Fahr. Double normalizing with the first treatment above the temperature of grain growth was considered, but was not employed because of the additional time and expense, and the fact that furnaces suitable for the high temperature treatment are not always available. Results obtained indicate that the single normalizing treatment is, in general, sufficient.

Heating for Quenching—The presence of scale on the specimen at the time of quenching can, of course, affect hardening to a substantial degree. It might seem preferable to heat in a lead pot, or in a controlled atmosphere, to prevent scaling. It was considered desirable, however, to heat in a manner more representative of general commercial practice, and also in a manner which could easily be used in any laboratory. Heating was, therefore, done in an electric furnace without any special atmosphere, the amount of scaling being controlled only by standardizing the time of exposure. The furnace was at temperature when the specimens were introduced, and the specimens were held in the furnace a total time of 40 minutes before quenching. Irregular scaling was sometimes encountered when specimens were placed directly on the hearth of the furnace, so the practice was adopted of supporting the specimens at the ends on racks made of saw blades.

Quenching Temperature—The quenching temperatures for hardening are those recommended for the various grades of steel in the A.S.M. Handbook.

Quenched Grain Size and Normalized Hardness—Along with the 4-inch specimen, a 1-inch specimen, cut from the same piece, was heated in the same manner as for hardening but was air-cooled, while the former was quenched. This shorter specimen was used for determining grain size at the quenching temperature and normalized hardness.

Quenching—All specimens in this investigation were quenched in water at 65 to 75 degrees Fahr. This is a temperature range which is commonly used in industry, and also one which can be easily attained in winter or summer. Consideration was given to special quenching devices with the object of duplicating conditions with respect to the flow of coolant. Experience has shown, however, that consistent results can be obtained without such devices. Special quenching apparatus is costly, is not generally available, and is difficult to reproduce exactly, even from identical drawings. The water used in quenching was not circulated, but vigorous stirring was accomplished by motion of the specimen itself during quenching.

Aging—It has been shown (6) that freshly quenched martensite of high hardness may increase measurably in hardness on aging or slight reheating, but any such increases were scarcely measurable during a day or so at ordinary temperatures in the steels tested.

Tempering—Some investigators have tempered or drawn the hardened specimens, at 500 degrees Fahr. for example, before testing. The present authors consider it more desirable to obtain hardness values on the specimens as quenched. Incidentally, any tempering treatment after quenching increases the time required for the test.

Cutting—The quenched specimen was cut in half transversely on an abrasive wheel with care to prevent heating. It might be thought that there is less chance of sufficient heating during cutting to affect the hardness in the case of a specimen tempered at 500 degrees Fahr. Actually, however, it is necessary in either case to prevent any measurable heating. Detection of accidental heating during cutting is more simple in the as-quenched specimens.

Surface for Testing—After the cutting operation, both ends of the half not gripped by the tongs were ground flat, parallel to each other and perpendicular to the axis of the specimen. The face representing the center of the original specimen was polished through

240 grain alundum on a wet wheel and etched in nital. This etching discloses irregular hardening or accidental overheating during cutting. It also facilitates marking. This surface was then scribed by means of a special tool with seven concentric circles $\frac{1}{16}$ inch apart and a point at the center. Four diameters were drawn so that the radii were 45 degrees from each other.

Hardness Tests—Rockwell C impressions were made at each intersection of a radius and a circle except for the inner circle where

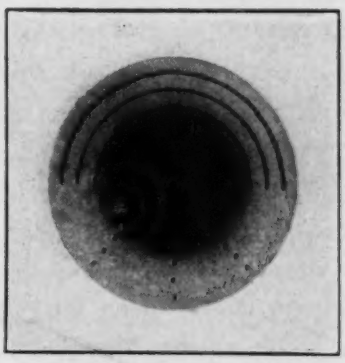

Fig. 3—Hardenability Specimen with Circles.

only four readings were taken on account of lack of space. (See Fig. 3). One reading was taken at the center. Tests representing the surface hardness of the specimen were made on the outer cylindrical surface $\frac{1}{8}$ inch from the prepared face and opposite the diameters drawn on that face. The outer surface of the cylinder was lightly ground or polished before testing to remove dirt and scale.

Surface Hardness—The value taken for surface hardness was the average of all consistent surface readings. Occasional values which appeared abnormally low were omitted in determining the average.

Center Hardness—Because of the chance of error in the single hardness reading at the exact center of the specimen, the value taken for center hardness was the average of five readings, including the center reading and the four readings on the innermost circle, which is only $\frac{1}{16}$ inch from the exact center.

Estimation of "Area"—The method of estimating the area under the curve directly from the hardness readings, and the formula used for this estimation, are shown in connection with Figs. 4 and 5.

Reproducibility of Results

In order to check the reproducibility of results, duplicate tests were run in many instances; no variation of more than plus or minus ½ Rockwell-Inch was observed for the area, while an average maximum variation of plus or minus 1 Rockwell point was observed for the surface and center values between the duplicate samples (from

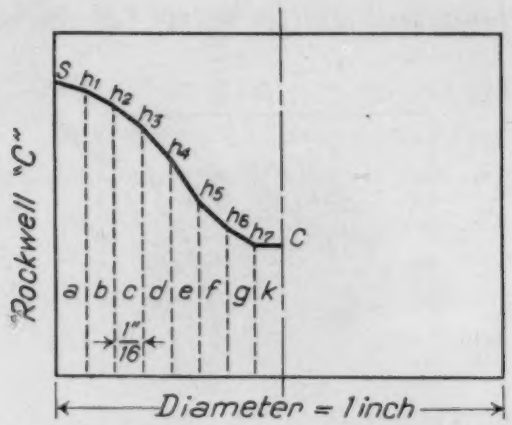

Fig. 4—Derivation of Formula for Area.

S = Surface Hardness.
h_1, h_2 etc. are hardness values at depths indicated.
C = Center Hardness

Area of "a" $= \frac{S + h_1}{2} \times \frac{1}{16}$

Area of "b" $= \frac{h_1 + h_2}{2} \times \frac{1}{16}$, etc.

Total Area (a + b + c + d + e + etc.)

$$= \frac{1}{16}\left(\frac{S}{2} + h_1 + h_2 + h_3 + \ldots + \frac{C}{2}\right)$$

Since the diagram represents only one-half of the full (symmetrical) hardenability curve the total area under the full curve is

$$= \frac{1}{8}\left(\frac{S}{2} + h_1 + h_2 + h_3 + \ldots + \frac{C}{2}\right)$$

	INDIVIDUAL READINGS								Avg.		O.
S	62	63	62	62	63	62	61	62	62	$\frac{S}{2}$	31
1	59	59	58	60	59	60	59	59	59	1	59
2	57	56	57	58	58	58	57⅝	58	57⅝	2	57⅝
3	54	56	54	53	54	54	53	54	54	3	54
4	39	40	39	41	39	39	40	39	39⅝	4	39⅝
5	32	33	31	31	32	33	32	33	32	5	32
6	29	30	29	29	29	30	30	30	29⅝	6	29⅝
7	29	28	27	28	..	..	..	..	28	7	28
C	28	..	..	..	..	..	..	..	28	$\frac{C}{2}$	14
Total Ordinates											344⅝
Total Ord. ÷ 8 = Total Area											43
Hardenability Rating									S 62	Area 43	C 28

Fig. 5—Card of Individual Readings.

the same billet) representing 46 different heats of steel. In the high carbon ranges, the surface error is less than in the low and medium carbon ranges because of the form of the maximum hardness vs. carbon curve (See Fig. 6); the figure given is the maximum variation.

To check periodically the reproducibility of results, a set of standard tests (S.A.E. 1045) was made from three bars rolled from the same billet, these standard pieces being normalized, machined, and cut to standard dimensions. In one bar there was a small amount of segregation, which made its hardenability curve slightly higher at the center than was observed for the other two bars. Each bar was separately identified, cut up into standard test pieces, and checked intermittently during the investigation; standard practice was maintained throughout. During the course of the investigation, these pieces were used as "standards" and, because of the slight segregation in each bar, served as sensitive checks on the uniformity of the procedure used. Tests were made by three different operators at different times, and of the 23 standard tests run, 21 checked within plus or minus ½ Rockwell-Inches for the area, the remaining two within plus or minus ¾ Rockwell-Inches. Surface and center averages were within plus or minus 1 Rockwell point.

The Rockwell tester was calibrated at regular intervals, and during the period of these experiments special care was exercised. Standard blocks were cross-checked frequently.

These 23 standard tests run at regular intervals by different operators afforded an accurate check on experimental procedure, and it is reasonable to assume in this investigation that variations greater than plus or minus ½ Rockwell-Inches for the area are due to characteristics of the steel and not to experimental error.

Hardenability Rating

As suggested early in this paper, a description of hardenability should, in general, answer two questions: (1) How hard will a steel harden? and (2) How deeply will it harden? The surface hardness, determined as described above, answers the first of these questions with respect to the size of specimen and quenching method employed. For the common carbon forging steels, the size and quenching method here employed result in meeting or exceeding the critical quenching velocity of the steel at the surface. The value of surface hardness then also represents the maximum hardness to which the steel can be hardened. A possible exception to this would be in the the case of

steels in which substantial proportions of austenite are retained on quenching, but this is not the case in the steels here under consideration.

Depth of hardening is indicated by the three values proposed for hardenability rating: Surface, area, and center, which, for convenience, we will abbreviate as the S-A-C rating. The area value alone does not describe the penetration effect. For example, the same area value might be obtained for an S.A.E. 1045 steel and for an alloy steel containing 0.30 per cent carbon. The 0.30 per cent carbon steel, however, would be softer at the surface and harder at the center than the S.A.E. 1045. When the surface and center values are considered together with the area value, the form of the hardenability curve is indicated rather completely.

In the opinion of the authors, the testing procedure and the method of rating and expressing results, which have been described, meet satisfactorily the requirements set forth above. This investigation has brought out facts regarding the effects of composition and grain size upon these hardenability factors which will now be discussed.

Maximum Hardness

The thought has been prevalent that all of the factors, that is, carbon, alloying elements, grain size, etc., associated with penetration or depth of hardening, are also those which determine the maximum hardness attainable on quenching. Herty (4) more recently has indicated a general relationship between the total chemistry of the steel and maximum attainable hardness, and has not considered grain size as a factor. It is well known that the degree of hardness attainable on quenching increases with carbon content. It occurred to the present authors that the hardness of martensite is determined by its carbon content, and that the effects of other elements and of grain size on quenched hardness result almost entirely from their effects on transformation rates. In other words, they felt that the maximum hardness attainable in a steel is determined by its carbon content alone, and that other elements, together with grain size, merely determine the ease or difficulty with which this maximum potential hardness can be attained.

Tests to be subsequently described, on specimens up to 3 inches diameter, showed that substantially the same surface hardness was obtained from ¾ inch diameter to 3 inches diameter in three steels

containing about 0.35, 0.45, and 0.75 per cent carbon, respectively. This indicated that maximum hardness was obtained at the surface of the 1-inch diameter rounds used in this investigation on at least a great many of the carbon steels tested. Steels of low hardening power tested by the authors, and also reported by other investigators, have obviously failed to give maximum potential hardness at the surface of 1-inch rounds quenched in water. This means that the cooling velocity at the surface of the 1-inch round was less than the critical quenching velocity for such steels.

To determine the relationship between carbon content and maximum hardness over a wide range of composition, special tests were made on specimens ⅜ inch in diameter, ground on two parallel faces to a thickness of ¼ inch. A parallel investigation was conducted in another laboratory by associates of the authors (7) on specimens prepared from wires about ¼ inch in diameter. In this study of maximum hardness, the hardening effect was intensified when necessary by the use of especially high quenching temperatures, and also by quenching in iced caustic solution. A carbon range from approximately 0.10 to 1.00 per cent was studied. For this purpose, steels from the following series were tested in the manner described:

S.A.E. 1000 up to 1.01 Per Cent Carbon
S.A.E. X1000 up to 0.28 Per Cent Carbon
S.A.E. X1300 up to 0.45 Per Cent Carbon
S.A.E. T1300 up to 0.35 Per Cent Carbon
S.A.E. 2100 up to 0.19 Per Cent Carbon
S.A.E. 2300 up to 0.20 Per Cent Carbon
S.A.E. 3100 up to 0.19 Per Cent Carbon
S.A.E. 4600 up to 0.16 Per Cent Carbon
S.A.E. 5100 up to 0.40 Per Cent Carbon
S.A.E. 6100 up to 0.39 Per Cent Carbon

The results obtained in both laboratories indicated a close relationship between the maximum hardness on the Rockwell C scale and carbon content, regardless of the presence or absence of alloy elements in the amounts present in the common S.A.E. steels. (See Fig. 6). This relationship holds, of course, only when the critical quenching velocity is reached or exceeded. For example, an S.A.E. T1335 and an S.A.E. 1035, with the same carbon content, gave surface hardnesses which were within ½ Rockwell point, under similar conditions of quenching and testing. Another interesting comparison is found in results reported by other investigators. McQuaid (8) obtained a hardness of 38 Rockwell C on the surface of a 1-inch round containing 0.11 per cent carbon and 3.17 per cent manganese.

Sykes and Jeffries (6) obtained the same hardness on a steel containing 0.11 per cent carbon, with only 0.62 per cent manganese, by quenching a ¼-inch square specimen in iced caustic solution.

Interesting features of the curve are the rapid increase in Rockwell hardness with carbon content in the lower carbon range, and the fact that a hardness of 60 Rockwell C was reached at about 0.39 per cent carbon. With respect to the higher carbon steels, in par-

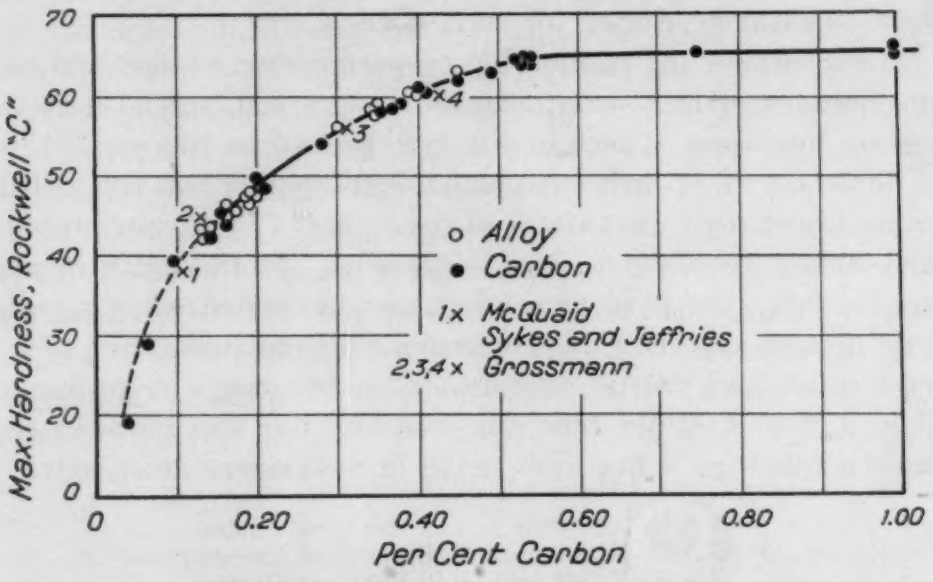

Fig. 6—Maximum Hardness vs. Carbon Content.

ticular, it is to be noted that the values for maximum hardness shown in the curve do not reflect the possibility of additional increases in hardness of a few points on the Rockwell scale by tempering at low temperatures with or without previous treatment at subnormal temperatures, as shown by Sykes and Jeffries (6).

In predicting the maximum hardness of a heat of steel, carbon variations throughout the heat and within individual ingots must be kept in mind. Furthermore, this hardness is presumably determined by the amount of carbon actually in solution at the quenching temperature, and would not be greatly affected by carbon in the form of undissolved carbides.

A note of practical interest is found by converting the Rockwell C values for maximum hardness to Brinell values (in accordance with the conversion tables published by International Nickel Company). It is observed that the Brinell hardness vs. carbon content relationship is approximately linear from 0.10 to 0.50 per cent carbon.

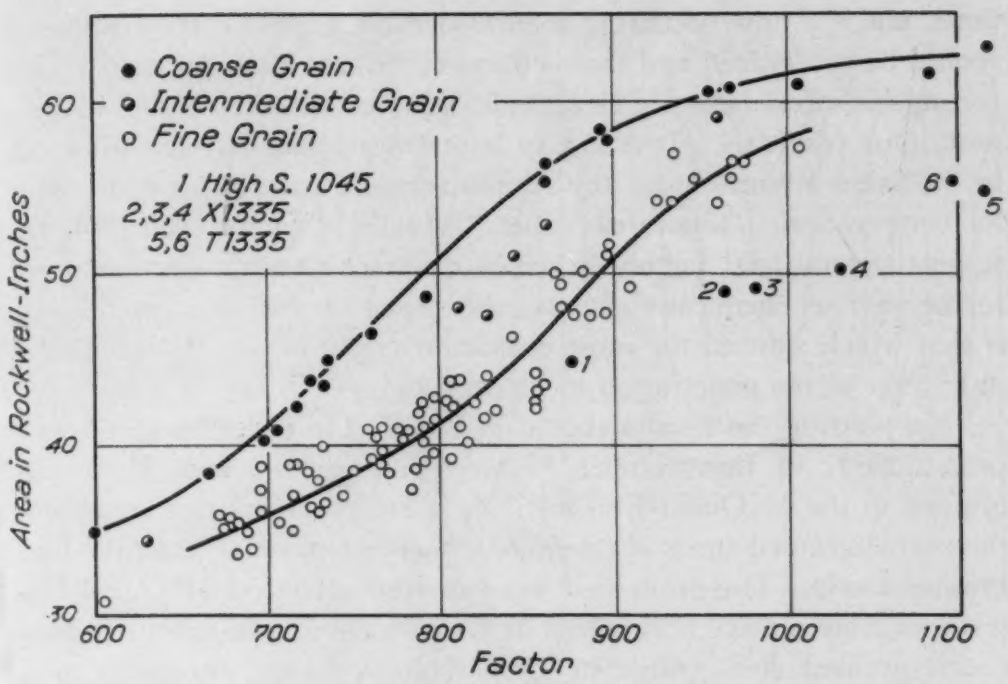

Fig. 7—Area vs. Factor (1000 C + 400 Mn + 500 Cr + 100 Ni + 100 Cu)

Depth of Hardening

In Fig. 7 the area values derived as previously described are plotted against a function of the chemical composition, which is expressed by the empirical formula 1000 C + 400 Mn + 500 Cr + 100 Ni + 100 Cu. This formula does not take into account P, S and Si because no definite effects seemed to be produced by variations in these elements within the range covered in the steels investigated (P — 0.016 to 0.030 per cent and Si — 0.190 to 0.300 per cent). The last three elements of the formula, Cr, Ni, and Cu, are the residual elements commonly found in commercial steels. These residuals, when present in substantial amounts, affect the hardenability characteristics and are, therefore, considered in the formula. Because of the nature of the raw materials used, there has been a general increase in the amount of residual chromium and copper in the past six years. Sullivan (9) has shown that the residuals vary considerably from plant to plant, as well as from year to year. The average residual chromium for all plants by tonnage capacity in 1929-1930, December-February, was 0.014; for January-December, 1936, the average was 0.029. These are average figures and it is expected that the variations would be much greater from plant to plant and from heat to heat. Since these residuals are subject to such varia-

tions, and are now occurring in considerable amounts, their presence should be recognized and their effects taken into consideration. This formula is offered merely as a guide based on the carbon and manganese, plus residuals. It is not to be expected that hardenability can be indicated accurately by any simple formula covering a wide range of composition. The area values actually obtained were plotted against several trial factors in which different weights were assigned to the various chemical elements; the factor or formula given above is that which showed the most consistent relationship. It is a useful indication of the penetration to be expected.

In plotting the results shown in Fig. 7, 116 different steels were investigated; of this number 85 were fine-grained and 31 coarse-grained in the McQuaid-Ehn test. It is evident from this curve that the coarse-grained steels are definitely deeper-hardening than the fine-grained steels. The grain size was rated both from a McQuaid-Ehn test and from a piece normalized at the quenching temperature. Most coarse-grained steels rated at 1700 degrees Fahr. were also quite coarse at the quenching temperature, although six were intermediate; those steels showing this mixed tendency are marked on the curve. From a consideration of this curve, it is apparent that in the medium hardening range a coarse-grained steel with a factor of 700 will have approximately the same area as a fine-grained steel with a factor of 800. Expressed another way, a coarse-grained steel in this range will have an area about 7 to 10 Rockwell-Inches greater than a fine-grained steel with the same factor.

It is noteworthy that the coarse-grained steels fall more directly on the curve than do the fine-grained steels, a fact which would not be expected if there were a wide variation in relationship between the McQuaid-Ehn rating of grain size and the austenite grain size at the quenching temperature. This may be due in part to the fact that these steels in the upper part of the curve have less sensitivity for the size (1-inch round) under consideration.

The core hardness on all the 1-inch rounds tested was always well above the normalized hardness, a fact which adds weight to the method of rating the depth of hardening.

Nineteen steels (S.A.E. 1040) with similar chemistry and grain size, but with different amounts of manganese, were compared, and it was observed that 20 points of manganese (between 0.50 and 1.00 per cent) increased the area by 4 Rockwell-Inches.

Incidentally, it is noteworthy that the high sulphur-high manga-

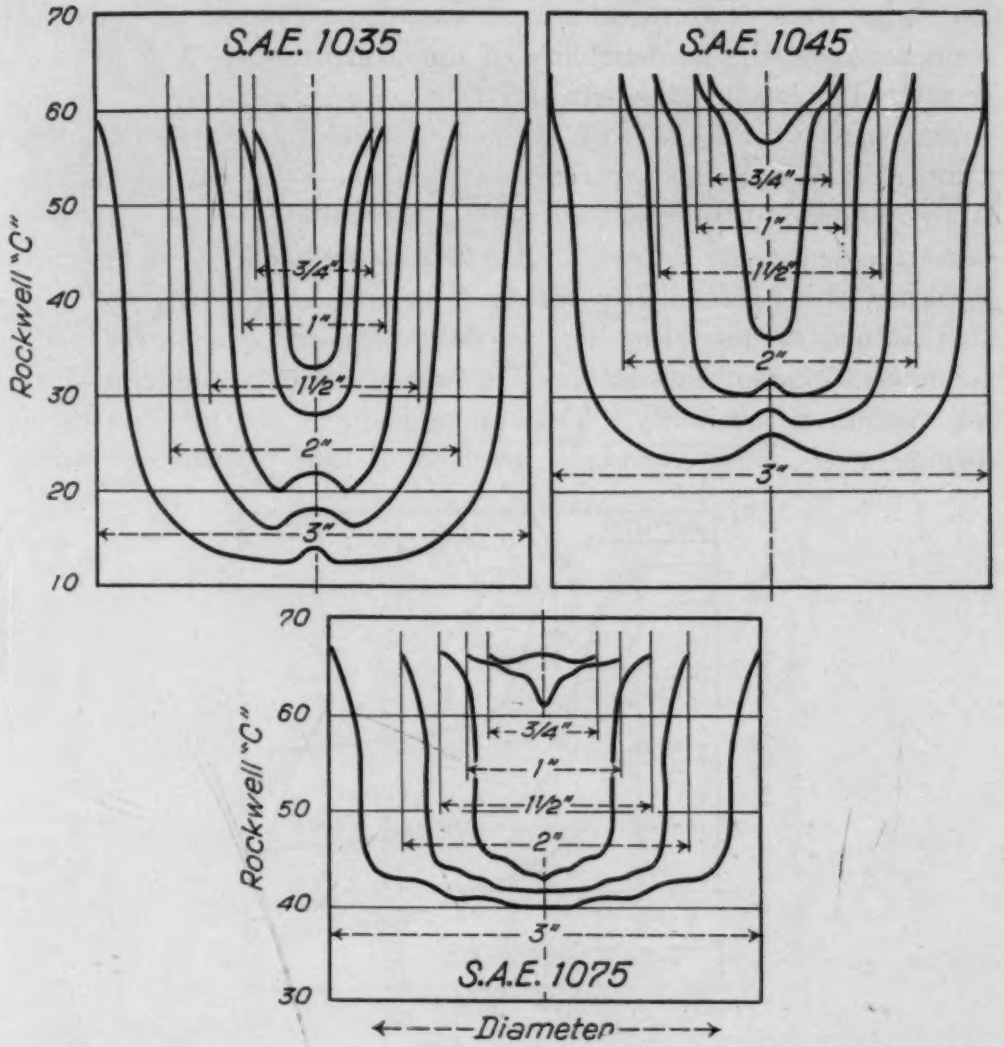

Fig. 8—Effect of Diameter on Depth of Hardening in Water-Quenched S.A.E. 1035, 1045, and 1075, of Fine-grained Type.

ANALYSES

	1035	1045	1075
C	.37	.48	.78
Mn	.78	.78	.77
P	.016	.016	.028
S	.032	.030	.031
Si	.229	.265	.188

nese steels show abnormally low depth of hardening by the formula. This is readily explained by the fact that the formula does not consider the effect of sulphur, which is, of course, to remove manganese from its solution and carbide forming effects by combining with it to form sulphide inclusions. As stated before, the sulphur, along with silicon and phosphorus, is within the ordinary limits in all other cases except where indicated. These steels are plotted merely to bring out this point.

Since there is a critical sample size, depending on the quenching conditions and the hardenability of the steel involved, which is most sensitive in revealing the area difference, we should expect, and have found, in comparing a large number of steels of different analyses, a considerable variation in area values over a certain chemistry range. Above or below this range the spread of values is less, merely because the sensitivity is less. The chemistry range, or, more strictly speaking, the *hardenability* range, in which the greatest spread of area values occurs (Fig. 7), is the range for which the 1-inch diameter specimen chosen for this investigation is the critical size for maximum sensitivity. This range includes the medium carbon forging steels most commonly involved in heat treating operations.

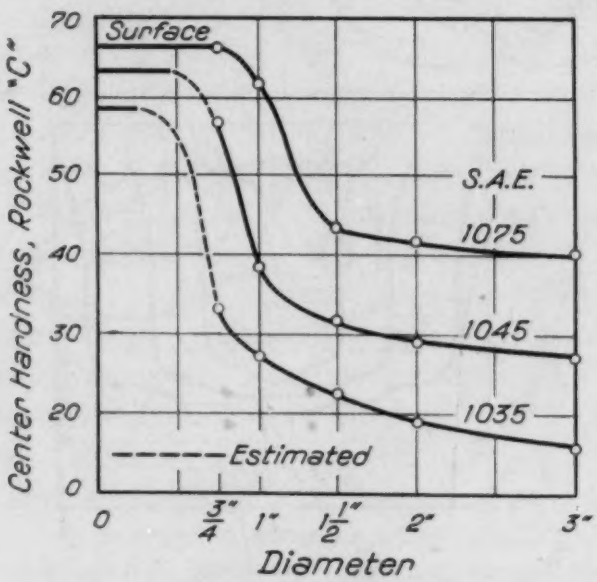

Fig. 9—Center Hardness vs. Diameter.

The Effect of Section

Provided that a sufficiently drastic quench is obtained to reach or exceed the critical cooling rate at the surface of any piece, the surface hardness obtained should be on or near the maximum hardness curve previously derived. That this is the case is shown in Fig. 8, for which S.A.E. 1035, 1045, and 1075 steels were water-quenched in various sizes from ¾ to 3 inches in diameter.

The surface hardness on all sizes quenched did not vary to any appreciable extent for each grade of steel so tested, the maximum hardness being obtained. The various sizes were forged down in each case from one billet.

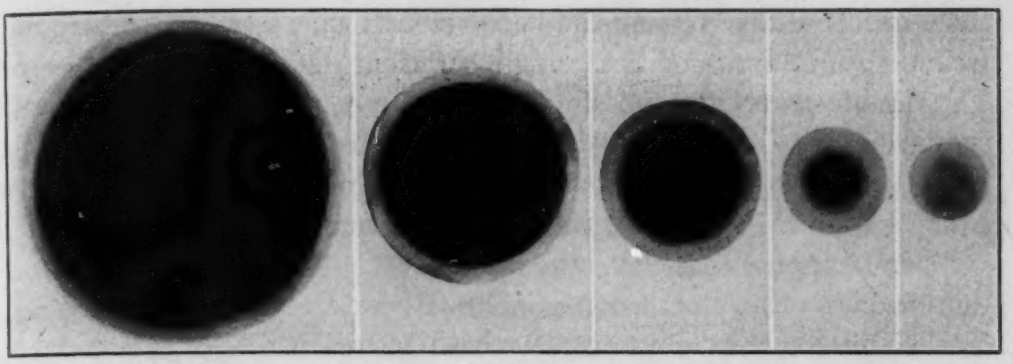

Fig. 10—Appearance of S.A.E. 1045, Water-quenched, Cut in Half and Etched. (3", 2", 1½", 1", ¾")

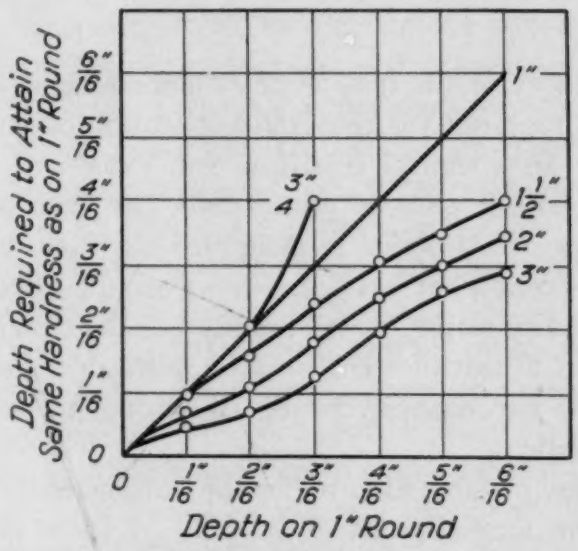

Fig. 11—Comparison of One-Inch Round with Larger Diameters—S.A.E. 1045.

A feature of this set of tests is the fact that, as previously stated, there is a certain size for every grade of steel at which the depth of hardening test is most sensitive and the diameter of this critical size increases as the hardening power of the steel increases. This is illustrated in Fig. 9, the dotted lines being estimated, since sizes smaller than ¾ inch diameter were not tested. The fact that full hardness is obtained at the surface of even the 3-inch rounds in the grades tested after an ordinary water quench differs from results given by previous investigators (10). Fig. 10 shows how the full-hardened rings appear, after etching in nital, for S.A.E. 1045 in the sizes quenched.

A practical application of work along this line lies in using the fact that for a given steel the hardness at various depths on larger

sizes can be derived from the hardenability curve of a 1-inch round, within certain limits of analysis, if sufficient data have been collected. Fig. 11 illustrates this possibility which, when established by a sufficient number of tests, is directly applicable to practical problems. Suppose, for example, it is desired to determine how far in from the surface of a 2-inch round the hardness remains above 45 Rockwell "C", and suppose that the standard test on a 1-inch round has shown this hardness to a depth of $\frac{3}{16}$ inch. By reference to Fig. 11 it will be seen that the same hardness would be reached approximately $\frac{1}{8}$ inch below the surface of the 2-inch round.

Discussion

The sensitivity of the test, as described above, is felt to be much greater than is required for practical application of steel. This is as it should be. In chemical analysis, for example, carbon can be determined to within plus or minus 0.01 per cent or one "point," whereas a range of 10 points is generally satisfactory for the selection of steel. From what has been shown of the effect of chemistry on the hardenability rating, it will readily be seen that ordinary variations throughout a heat of steel, or even within one ingot, will cause variations in the hardenability rating amounting to several times the experimental error.

The greatest possible area under the hardenability curve is equal to the maximum attainable hardness ($H_{max.}$) times the diameter of the specimen. This hypothetical value, which may be designated $A_{max.}$, is the area under the curve for a specimen that would quench to $H_{max.}$ from surface to center. The ratio of the actual area A to $A_{max.}$ that is $\left(\frac{A}{A_{max.}}\right)$ may be used as a convenient measure of penetration effect in general, and of the contribution of specific alloy elements to that effect.

"Distortion" in hardening is commonly associated with austenitic grain size. It seems to the authors that it might be more properly associated with hardenability, and that the systematic use of quantitative hardenability data in distortion problems should be valuable.

Conclusions

1. To describe the "hardenability" of a steel, two factors should be measured and expressed: (1) the maximum hardness attainable

on quenching, which will be referred to as $H_{max.}$, and (2) the "penetration" effect.

2. $H_{max.}$ is shown to depend solely on carbon content, regardless of alloys in amounts present in the common S.A.E. steels, and regardless of austenite grain size.

3. $H_{max.}$ is attained when quenching conditions are such that the critical cooling velocity of the steel is reached or exceeded (providing that austenite is not retained in substantial proportions).

4. The critical cooling velocity is a characteristic of the steel, and is determined chiefly by (1) carbon content, (2) content of alloy elements other than carbon, and (3) austenite grain size.

5. The hardness values at the surface and at various points within a quenched piece of steel define the penetration effect. These values approach $H_{max.}$ (which is determined by the carbon content of the steel) as the *actual* cooling velocities at the respective points in the piece approach the critical cooling velocity characteristic of the steel. Some typical curves are given which show for specimens of different diameters the depths below the surface at which equal hardness values are attained on quenching.

6. General use of a standard method of hardenability testing, and a standard method of expressing results, would greatly assist the scientific solution of practical heat treating problems.

7. A test previously used chiefly for research purposes to illustrate differences in a *qualitative* manner, has been examined critically and found suitable for the regular testing of steels whose applications justify close control of hardenability, and for the description of hardenability in *quantitative* but simple terms.

8. The proposed method of rating hardenability consists in stating (1) the surface hardness, (2) the area under the hardenability curve, and (3) the center hardness. For convenience, this may be referred to as the "S-A-C" rating.

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DISCUSSION

Written Discussion: By A. S. Jameson, metallurgist, International Harvester Co., Chicago.

We are in agreement with the authors that a standardized quantitative hardenability test such as they propose would be desirable and they should be complimented on the thorough way they have acquired and presented their data.

Let us now see how the quantitative hardenability test can be put to practical use. We have an actual problem: A 5-inch diameter splined bore gear is made from S.A.E. 1045 steel and heat treated to a hardness of 40-50 RC. The chemical composition and McQuaid-Ehn grain size of the steel used is specified—carbon 0.40-0.45, manganese 0.60-0.90, chromium 0.10 (max.), McQuaid-Ehn grain size 1-4. It is desired to change this material and specify a fine grain steel. Experience will first be called upon to give us a general guide as to the proper road to take, and perhaps we shall consider that in order to compensate for the proposed change in grain size the carbon or manganese content, or both, should be increased, or a small chromium addition should be made. We do not believe that experience alone would be relied upon to make this change which would involve many thousands of this and similar parts without some preliminary investigation using gears as test specimens to determine what percentage of carbon, manganese or chromium must be added to fine grain steel to make its hardenability equivalent to the coarse grain steel. Here the problem is solved by heat treating actual parts.

Should the authors test prove to be practicable, the problem could be solved in a simpler manner by tests on 1-inch rounds and if they further show that a formula based on chemical composition and McQuaid-Ehn grain size can be evolved then it would not be necessary to even produce steel before a solution were arrived at.

We have selected from various heats which were used in this actual test three heats which we considered as being most suitable for use in checking in a limited way, of course, the reliability and practicability of the tests proposed by the authors. The chemical composition and McQuaid-Ehn size of these heats was as follows;

Table I
Chemical Composition and McQuaid-Ehn Grain Size

		Steel		
	Element	A	B	C
Chemical Composition	Carbon	0.38	0.45	0.46
	Manganese	0.72	0.86	0.70
	Sulphur	0.028	0.033	0.026
	Phosphorus	0.022	0.021	0.012
	Silicon	0.20	0.20	0.27
	Chromium	0.30	0.25	0.04
	Copper	0.05	0.04	0.07
	Nickel	0.10	0.10	0.07
McQuaid-Ehn Grain Size		7	7	2

As to normality, the steel "C" was quite normal, steels "A" and "B" would be considered by some as being slightly abnormal inasmuch as the cementite grain boundaries were not continuous, the pearlite areas were, however, quite normal.

From tests on actual parts, it was concluded that the hardenability of the steels was in the following order: B, C and A. B represents one of those heats of steel which is unfortunately not rare, it has chemical and physical characteristics which make it a border line between oil hardening and water hardening for this particular application. Steel C has the same carbon content as B and is a coarse grain steel containing no chromium. Steel A is a fine grain steel with a lower carbon content than B.

1-inch rounds 4 inches long were machined from 2-inch round hot-rolled bars of the three steels. The specimens were machined off center. They were prepared in a manner similar to that described by the authors. The heat treatment given these specimens is described below.

The nine specimens were heated to 1650 degrees Fahr., held 35 minutes and cooled in air. (Total time in furnace 60 minutes).

Two specimens from each bar were placed in an oven type gas-fired furnace at 1550 degrees Fahr., held for 45 minutes, (time at heat 35 minutes) and quenched in water (66 degrees Fahr.). One specimen from each bar was placed in a furnace with atmosphere control at 1550 degrees Fahr., held for 50 minutes (time at heat 35 minutes) and quenched in water (66 degrees Fahr.). The atmosphere was controlled by dripping into the furnace a specially compounded oil at the rate of 50 drops per minute.

We were interested in the authors' references to furnace atmosphere. These specimens were hardened in two different types of furnaces. We might say that one set of specimens was heated for hardening in an "oxidizing" atmosphere and the other in a "reducing" atmosphere.

The specimens were not tempered. We do note, however, that the authors consider it more valuable to obtain hardness on specimens "as quenched." With 1-inch rounds hardenability specimens made from carbon tool steels, especially where the surface is ground for surface readings, tempering at approximately 500 degrees Fahr. is desirable to prevent cracking of the test pieces.

The authors do not state how the specimen was prepared for surface hardness readings. We propose that surface hardness readings be taken after removal of approximately 0.008 inch from the curved surface of the hardened speci-

men and that the surface hardness be taken as the mode of 50 readings rather than as the average of 50 or a less number of readings or by eliminating "wild" readings.

We show below evidence to support our contention that an unground surface should not be used for hardness readings.

Table II
Hardness Frequency

	Reducing Atmosphere			Oxidizing Atmosphere					
				A		B		C	
Rockwell "C"	A 1	B 1	C 1	1	2	1	2	1	2
Unground Surface									
64	..	..	..	..	..	..	..	..	..
63	..	..	..	..	..	..	..	1	..
62	..	..	..	..	..	5	3	5	10
61	..	..	..	2	..	8	3	9	7
60	..	..	..	5	..	7	7	8	6
59	..	..	..	11	4	13	12	3	10
58	..	..	..	11	10	5	8	5	2
57	..	2	..	4	10	7	5	3	4
56	..	4	..	9	10	3	9	5	4
55	9	2	3	5	7	..	2	..	1
54	7	8	11	2	9	..	1	..	4
53	11	6	12	..	..	1	..	..	2
52	11	10	12	..	..	1	..	..	..
51	8	8	6	..	..	..	..	..	..
50	1	2	5	..	..	..	..	..	..
49	2	5	..	..	..	..	..	..	..
48	1	1	..	..	..	..	..	..	..
47	..	..	1	..	..	..	..	..	..
46	..	2	..	..	..	..	..	1	..
Ground Surface									
64	..	..	..	..	1	..	..	..	..
63	..	6	6	..	3	5	..	11	14
62	..	17	19	..	2	21	19	17	20
61	6	13	18	5	4	20	16	15	7
60	12	10	7	14	13	4	11	7	4
59	16	2	..	18	20	..	1	..	5
58	9	2	..	10	7	..	3	..	..
57	7	..	..	3	..	..	..	..	..

Table III
Hardness Averages

Number of Readings	Reducing Atmosphere			Oxidizing Atmosphere					
				A		B		C	
	A 1	B 1	C 1	1	2	1	2	1	2
Unground Surface									
10	53.1	51.6	51.7	57.9	56.9	58.3	58.4	57.1	59.2
20	53.5	52.2	52.4	57.9	56.8	58.4	58.8	58.8	59.5
30	53.4	52.3	52.6	57.8	56.7	58.3	58.7	58.9	59.2
40	53.0	52.2	52.5	57.8	56.4	58.7	58.6	58.6	59.4
50	52.8	52.1	52.5	57.7	56.5	58.9	58.4	59.0	58.4
Ground Surface									
10	59.2	61.8	61.4	59.3	59.0	61.4	60.6	61.2	61.4
20	59.2	61.8	61.6	59.4	59.1	61.4	60.8	61.4	61.6
30	58.4	61.4	61.6	59.3	59.1	61.4	61.0	61.6	61.7
40	58.6	61.2	61.5	59.3	60.0	61.5	60.9	61.6	61.8
50	58.6	61.2	61.5	59.3	60.8	61.6	60.9	61.6	61.7

It is interesting to note that hardness readings taken on an unground sur-

face are lower for specimens treated in a reducing atmosphere. This is explainable when we consider that a certain degree of decarburization would occur in the normalizing operation. This decarburization would be removed by scaling in the oxidizing atmosphere, but not in the reducing atmosphere. The authors mention that the scale condition on the surface would affect the surface hardness, it is of course true that a scale that will break off in the quenching bath is to be preferred to one that clings to the surface, i.e., one produced or maintained by an excessively reducing atmosphere.

Attention is called by the authors' statement that surface (sub-surface) hardness is controlled at least in carbon steels by the carbon content alone. This is certainly true and is supported by the previous data.

Hardness penetration readings were taken in a manner described by the authors. We have ourselves been using for the examination of carbon tool steels a fixture illustrated on the next page which is very convenient.

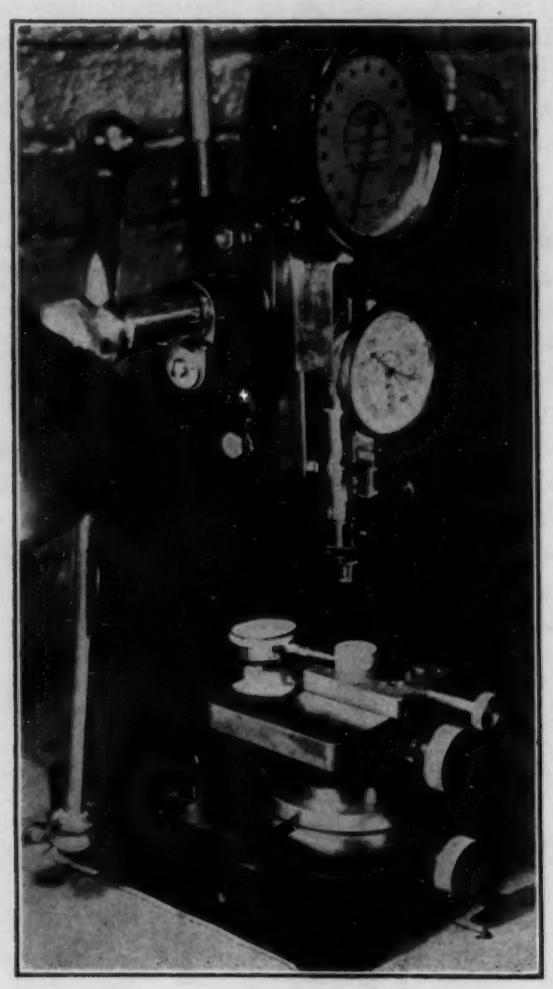
Table IV
Hardness Penetration Readings

	Reducing Atmosphere					Oxidizing Atmosphere									
	1					1					2				
	1	2	3	4	Av.	1	2	3	4	Av.	1	2	3	4	Av.
1	55	57	56	55	55.7	56	55	56	56	55.7	55	56	54	55	55.0
2	55	53	54	54	54.0	54	53	55	54	54.0	53	54	53	54	53.5
3	51	51	51	52	51.2	48	50	53	51	50.5	48	48	49	50	48.7
4	47	46	47	47	46.7	45	46	48	46	46.2	45	45	46	47	45.7
5	44	43	44	43	43.5	44	42	44	42	43.0	42	43	42	44	42.7
6	42	41	43	42	42.0	41	40	41	40	40.5	41	43	41	41	41.5
7	41	42	41	41	41.2	41	40	40	41	40.5	41	41	41	41	41.0
C	38	..	..	..	....	41	..	..	..	....	40	..	..	..	....
						B									
1	57	59	58	59	58.2	59	59	59	58	58.7	58	59	58	58	58.2
2	57	58	56	59	57.5	58	58	58	57	57.8	58	58	57	57	57.5
3	55	57	57	57	56.5	57	55	56	55	55.7	56	57	55	56	56.0
4	54	53	55	54	54.0	54	54	55	53	54.0	53	54	53	54	53.5
5	52	53	54	53	53.0	51	51	53	52	51.7	51	53	51	52	51.7
6	50	51	51	52	51.0	50	51	51	51	50.7	51	52	50	51	51.0
7	50	51	51	50	50.5	50	50	50	50	50.0	51	51	50	51	50.7
C	45	..	..	..	....	46	..	..	..	....	49	..	..	..	....
						C									
1	59	60	59	59	59.2	56	58	57	58	57.2	56	60	56	56	57.0
2	59	59	59	59	59.0	55	58	55	57	56.2	54	59	55	54	55.5
3	56	56	57	57	56.5	54	56	54	56	55.0	50	55	53	52	52.5
4	55	54	55	55	54.7	56	53	53	52	53.5	47	52	48	51	49.5
5	53	51	52	52	52.0	50	48	52	49	49.7	46	48	48	49	47.7
6	51	52	51	51	51.2	45	45	47	48	46.2	45	46	47	48	46.5
7	51	50	51	49	50.2	44	43	45	45	44.2	46	47	47	47	46.7
C	49	..	..	..	....	43	..	..	..	....	46	..	..	..	....

The S-A-C ratings of these steels A, B and C are given in Table V and their hardenability as determined by this method is in actual order as we found them to be in practice.

Table V
S-A-C Ratings

Reducing Atmosphere			Oxidizing Atmosphere					
A	B	C	A		B		C	
1	1	1	1	2	1	2	1	2
59-48-38	62-57-45	62-55-49	59-47-41	59-47-40	62-54-46	62-54-49	62-52-43	62-51-46



It will be noted that the S-A-C ratings as to area for the specimens hardened in the reducing atmosphere are greater. Sufficient data are not presented for any conclusions to be drawn.

The authors make some remarks relating to distortion and point to hardenability as predominating over austenitic grain size. This is open to demonstration. We present below data obtained from bore measurements taken on gears.

Table VI
Frequency of and Average Size Change (Minus) on Gear Bores

Inches of Change	Frequency			Average		
	A	B	C	A	B	C
0.001	3	10	..	.....	.....	.....
0.002	10	12	6	.....	.....	.....
0.003	9	8	10	0.003	0.002	0.004
0.004	7	4	13	.....	.....	.....
0.005	6	..	7	.....	.....	.....
0.006	..	..	2	.....	.....	.....
0.007	..	..	..	.....	.....	.....
0.008	..	..	1	.....	.....	.....

We regret that a limited time prevented us from drawing on or obtaining more data. We will in the future be very interested in following the progress of this proposed quantitative hardenability test.

Written Discussion: By E. O. Dixon, Ladish Drop Forge Co., Cudahy, Wisconsin.

The authors are to be complimented upon having presented in an able manner a plan of procedure for evaluating hardenability which may prove widely useful to makers and treaters of steel.

They have crystallized into an accurate practical plan a method for determining directly, quickly and economically those properties of steels that are of great importance in the application and treatment of individual mill heats of material. Up to the present time, the suitability of steel of a standard range of composition for development of desired physical properties by heat treatment has been estimated principally from actual chemical composition and austenite grain size. It is generally recognized that at best this indirect method not infrequently yields erroneous results. Furthermore, it is costly and slow. Hardenability tests have been used for a number of years, but, with a few notable exceptions, such tests have been highly specialized, with the result that findings in various cases were not comparable on any simple basis.

With a simple standard measurement of hardenability characteristics readily available, each user's requirements can be determined in units universally understandable, much to the advantage of the producer and consumer of steel which is to be heat treated. These characteristics should not be considered as possibly displacing chemical requirements, but as offering a means of classifying mill heats more closely in terms of their physical potentialities.

The comprehensive manner in which the general problem has been studied and reported is particularly commendable.

Written Discussion: By F. F. Vaughn, Caterpillar Tractor Co., Peoria, Illinois.

The authors are deserving of commendation for the capable manner in which their data have been prepared and presented in their paper dealing with hardenability measurements.

It is increasingly apparent that a knowledge of the hardenability characteristics of steel is important from the standpoint of practical heat treating operations, and is necessary if consistently uniform physical properties are to be attained in heat treated parts made from different mill heats of steel. The intelligent application of steel to such parts, therefore, creates a necessity for a standardized routine method for actual quantitative measurement and expression of hardenability. Accordingly, the proposed method and suggestions of the authors are worthy of earnest consideration by those concerned with the production of steel and steel products.

The proposed method of rating hardenability consists of stating (1) the surface hardness, (2) the area under the hardenability curve and (3) the center hardness. This method of rating does not, however, indicate the hardness at any point between the surface and center. It has been our experience that such information is of importance in the selection of material for certain applications requiring a considerable degree of overall toughness in

conjunction with a high degree of hardness for a definite depth below the surface as well as on the surface. We have also observed a characteristic of some steels, when quenched and drawn in heavy sections, to show an area of increased hardness at a depth just below the surface, the depth at which the increase occurs varying with different mill heats of steel. It may be desirable to take advantage of this hardness increase for wearing surfaces on parts machined after heat treatment.

We feel, therefore, that any method of rating or expressing hardenability should also indicate the hardness at one or more points between the surface and center.

In paragraph 1, of the sixteenth page, the authors state that a factor derived from a formula based upon chemical composition is a useful indication of the penetration to be expected. Examination of the curve for fine-grained steels in Fig. 7, indicates from our experience, that the actual hardenability values plotted for medium carbon steels with a factor of approximately 800, show such a spread as to make any predictions from the curve unsatisfactory for the largest and smallest parts we make from this type of steel.

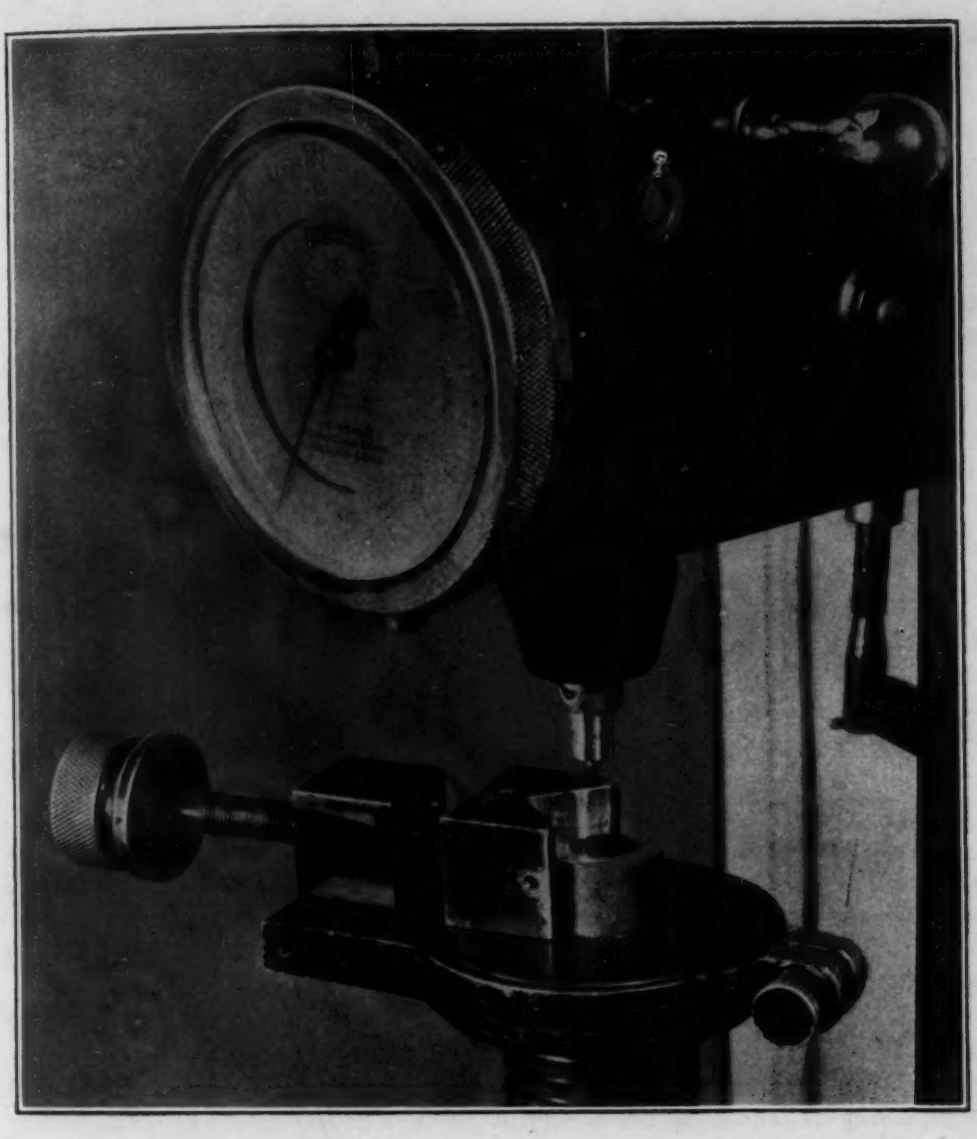
Written Discussion: By E. C. Bain and E. S. Davenport, United States Steel Corporation, Kearny, N. J.

This method of Burns, Moore and Archer for reporting hardenability in terms of three numbers may be expected to be attractive to many metallurgists because of its simplicity. Inasmuch as it may be adopted for use, either in its present or in some modified form, it seems advisable to make comments at its first presentation in order that any suggestions of supposed merit relating to the method may actually accompany the article. A few suggestions occur to the present discussers.

1. It may be helpful to point out that in the test on the 1-inch round the figure designated by the authors as "area" or "area under the hardness curve" is really the average hardness across the specimen; indeed, the refinement of assigning only half weight to the surface and center readings, which in their nature dominate half as much of the diameter as other readings, is a device properly employed in making correct averages. The three numbers to be set down in the reporting of the hardenability become then (1) surface hardness, (2) average hardness and (3) center hardness. The accuracy of the average hardness figure depends upon the number of concentric circles investigated. The present discussers having had extensive experience with this form of testing over the past six or more years, greatly prefer a larger number of readings—about 25 to the inch—and avoid additional consumed time by using a time-saving device to be described later.

2. The higher hardness found at mid-section in the very center of a water-quenched 1-inch round can scarcely be the result of more rapid cooling, and the authors may wish to reconsider their suggested hypothesis. Unless one is prepared to assume that heat may flow from a colder to a warmer zone, the rate of cooling through the important temperature range (from A_3 or Acm to about 900 degrees Fahr.) must always be lower in any given zone than in a more exterior zone, and this will apply even to the center of the specimen. Doubtless segregation, of no practical significance, causes the effect.

3. We abandoned the method of drawing concentric circles some years



ago and instead place the unmarked specimen directly against a jig on the anvil of the Rockwell tester, which makes it possible to make readings automatically, and precisely located, on concentric circles by turning a screw of known pitch, (24 or 25 threads per inch). The device attached to the anvil provides that the specimen be in contact with two vertical sides of a V-shaped guide whose angle is bisected by a line passing directly under the center line of the diamond penetrator. This device saves sufficient time to permit readings on more circles, adding useful knowledge of hardness distribution.

4. For those who do not possess cut-off machines of the type described in the paper an alternate method should be offered. Furthermore, it is difficult to avoid some softening by tempering during cut-off in some steels. The alternate method is to machine a shallow, but very sharp groove midway between the ends of the round before heat treatment and then break the round after hardening. Grinding down the fracture surface until the full diameter

of the round is exposed produces a transverse section with the same hardness distribution as in the method using a cut-off wheel.

The authors should perhaps counsel the staggering of the Rockwell impressions, avoiding placing them consecutively on actual radii of the section. Especially is this important when the more informative use of 12 circles, including the surface, is adopted in place of 8. The present discussers have never subscribed to the practice of the authors, of which they state that "occasional values which appeared abnormally low were omitted in determining the average," except where the penetrator actually entered a hardening crack or other obvious defect. It is difficult to know which readings are "abnormal"; perhaps, indeed, none are.

The authors' Fig. 6, in which is shown the influence of carbon content on maximum hardness attainable on quenching, is an interesting and useful contribution to the subject. It reduces to a more or less quantitative basis a fact, which of course, has long been appreciated and recognized by investigators working on hardenability problems.

One remarkable feature of the authors' work is illustrated in their Figs. 8 and 10 in which they show that full martensitic hardness was obtained at the surface of 3-inch diameter rounds of S.A.E. 1035 and 1045 steels. We would be interested to know if others have observed this and whether the authors have any explanation for their own results on this point since previous investigators, cited by the authors, apparently have been unable to obtain any such full-hardening action at the surface of large-diameter specimens of these relatively low-carbon steels.

The authors are to be complimented upon suggesting a useful short designation for hardenability in steels amenable to the method. The points of the technique are particularly well made and lucidly described.

Written Discussion: By W. H. Mayo of the U. S. Steel Corporation Research Laboratory, Kearny, N. J.

In addition to giving us a review of the subject of hardenability, the authors have proposed a method of representing the characteristic hardenability of a heat of steel in numbers, by applying a new unit, the Rockwell-inch, to an accepted way of indicating the hardenability of a cross section of steel. Their suggestion will receive the serious consideration of those who are interested in controlling the factors affecting hardenability. However, although the results of the test are expressed numerically, it should be borne in mind that the method is not *quantitative* in the full sense of the word. Furthermore, allowances will have to be made for the effect of prior mechanical and heat treatments on the grain size characteristics, the effect of various types of scale on the rate of cooling, differences in quenching technique, and numerous other variables when the test is carried out by different laboratories. In fact, the data reported in Fig. 8, when considered in the light of possible differences in grain size and quenching technique, do not necessarily contradict the results obtained by Grossmann referred to by the authors. The reaction rate of Grossmann's 1045 steel and the quenching technique he used were such that, in sizes over 1 inch in diameter, the critical cooling rate was never exceeded, even at the surface; therefore, in all probability, the structure at the surface was fine pearlite or fine pearlite and martensite, thus giving hardness values far below that of a

fully martensitic structure which is formed in steel only where the critical cooling rate has been attained or exceeded.

With regard to the length of the hardenability specimen, experience at our laboratory has shown that for 1-inch rounds a length of 2¾ inches is adequate when the proper technique is used.

We regret that the authors did not state the actual quenching temperatures used as well as the grain size developed at those temperatures, and referred merely to the A.S.M. Handbook where a range of temperatures is given. Moreover, inclusion of their comparative data on McQuaid-Ehn grain size and normalized grain size would have been helpful, for they do not clearly state how the grain sizes indicated in Fig. 7 were determined and classified.

It is interesting to note on page 16 that the effect on the hardenability of a change from "fine" to "coarse" grain is approximately equivalent to an increase of 40 points of manganese. This confirms, in general, our experience with regard to the comparative effect of grain size and of manganese on the critical cooling rate and hardenability of carbon steels.

Another point of interest is brought out by Figs. 8 and 10. On the basis that the temperature distribution through a piece of steel is determined by the heat diffusivity of the steel, it follows directly that, for a given set of quenching conditions and a given steel, the depth of hardening should be inversely proportional to the square of the diameter. This is confirmed by measurements on the rounds shown in Fig. 10 and by Fig. 8 (choosing RC 60 as "hardened" for S.A.E. 1045). When the ratio, $\frac{\text{depth of hardening,}}{\text{diameter}}$ is plotted against $\frac{1.}{(\text{diameter})^2}$ a straight line can be drawn through the points. This line can be determined for a steel by quenching two or more rounds of different diameters; then by extrapolation the diameter at which the steel will harden to the center may readily be found.

Oral Discussion

R. S. ARCHER: First, I would like to express on behalf of the other authors and myself our appreciation of the contributions brought out in the discussion, many of which I feel are very helpful.

Two of those who discussed the paper have brought up the matter of rejecting certain values in obtaining hardness. Dr. Bain and Mr. Davenport appeared to feel that that practice has been used in general, although I think Mr. Jameson noted more particularly that it referred only to surface readings. The actual statement in the paper is that occasional values were rejected in the case of determining average surface hardness only. I think we agree in that practice with the other speakers. The values rejected are, I think, about the same ones that Bain and Davenport would reject where there is some flaw or piece of adhering scale, or something of that sort to account for an erratic value.

Mr. Jameson's proposed grinding of the surface to obtain these values would increase the accuracy. As stated in the paper, we did more or less polish the surface by hand with emery cloth, again with the object of speeding up the process and avoiding the use of grinding equipment. As a matter of fact, as

far as the area values are concerned, a slight variation in the surface readings is not very important anyway. To determine whether the surface has hardened uniformly it would be desirable to make a much more careful survey.

Mr. Vaughn remarked that the area cannot always be predicted with sufficient accuracy from the chemical composition and grain size as indicated in the formula. This is, of course, the reason for proposing actual hardenability tests. Most of the steels do in our experience line up fairly well with this formula and with the grain size, especially where the specimen on which the test is run is carefully examined itself for analysis and for any possible segregation.

It is pointed out in the paper that the ordinary variations in chemical analysis throughout any commercial heat of steel, or in fact throughout any one ingot—and that does not include the part of the ingot that is customarily discarded—variations in analysis within the part of the ingot which commercially must be used are sufficient to give considerable variations in Rockwell-inches for the area. The test as stated is more sensitive than a great many heat treating jobs require, just as determination of carbon within plus or minus one point is closer than many jobs require where carbon content is the criterion of satisfactory use.

It is also mentioned in the paper that carbon content, alloy content and grain size are the chief factors affecting hardenability; it is suggested that perhaps any additional factors may be of somewhat less importance than these because it is natural that the factors of greatest importance would be discovered first. We do feel, however, that there are one or two other factors besides those three which affect hardenability to some extent.

Mr. Vaughn's comment that more information is needed about the form of the curve represents a thought which was considered. In some cases probably the actual form of the curve may be needed, although again it would be important to know whether that form was typical of a heat as a whole or merely of the particular specimen representing a particular ingot location which was used for the test.

The area value does, however, suggest the form of the curve in a rather general way because with a given value of surface hardness and center hardness a high area value indicates that the shoulders of the curve come out some distance, whereas a low area value with the same surface and center values would indicate a more rapid decrease in hardness toward the center of the specimen.

The data used for obtaining these expressions of course make it possible to plot the entire curve or to survey the chart and examine the readings.

We feel that for general heat treatment problems the three numbers are sufficient, and are numbers such that they can be transmitted very rapidly without the necessity of taking time to plot or transmit actual diagrams.

I understand that one of the points raised by Mr. Vaughn was the discovery of a region, after tempering at certain temperatures, somewhat beneath the surface at which there is apparently an abnormal increase in hardness. In other words, the distribution of hardness across a specimen drawn, for example at 1000 degrees Fahr., is not at all parallel to the hardness as quenched. We have found indications of the same thing, and we are hoping in fact to carry out

tempering tests on a good many of the specimens which are still remaining from this work so we can see hardness curves on the same specimens drawn at various temperatures.

Authors' Written Reply

The authors greatly appreciate Mr. Jameson's timely comments; they seem especially significant in view of the actual work carried out in checking the SAC test. The factors of the three steels mentioned are A—833, B—933 and C—774 (coarse grain). Reference to the curves presented in Fig. 7 rates the hardenability of these steels in the order B, C and A; it is interesting to note that Mr. Jameson's actual tests confirmed this.

With respect to the manner of taking surface readings we are in general agreement with Mr. Jameson. We did, however, state that the surface was "lightly ground or polished before testing to remove dirt and scale." This actually removed about 0.006-0.010 inch from the diameter. Checking of abnormal readings on numerous samples revealed that overheated spots, spots to which scale had adhered, or decarburization were the chief causes, in the order given. Such "wild" readings were therefore discounted. Usually 24 readings on the surface will suffice, three in each radius. We always normalized the forged bar, and machined afterwards; decarburization on the test surface was, therefore, light since the piece was at a decarburizing temperature less than 40 minutes.

We are pleased to note Mr. Jameson's confirmation of our belief that surface hardness (providing the critical rate is exceeded and there is little or no austenite retained) is dependent on carbon alone. This we found to be true in low alloy as well as carbon steels. A hundred and more hardenability tests run since the original data was compiled have borne this out. In fact, tests which gave too high a surface hardness for the carbon content as determined across the face were checked for segregation effects and the true surface carbon content was found to be that indicated by the maximum hardness curve. The close checking of the SAC ratings on all three steels in an "oxidizing" atmosphere is worthy of note. This is even more significant in view of the fact that Mr. Jameson took but four readings in each circle whereas the authors took eight.

Mr. Dixon's kind comments will, we hope, be justified. This problem of rating hardenability has been attacked from many angles; the ultimate goal is, of course, the standardization of a simple test which will eliminate much of the type of testing so tediously carried out heretofore. This proposed test was offered as a step towards putting hardenability on a basis whereby both the producer and consumer of steel could speak in definite terms.

Mr. Vaughn's thoughts concerning the desirability of giving more than three figures for a hardenability rating is interesting; for exact or special applications perhaps an S-1-2-A-C rating or modification of the same could be used. Since the rating of the 1-inch round is used merely as a standard the requirements of a particular job would have to be evaluated on the basis of comparative tests; once established the SAC rating alone should generally suffice.

Mr. Vaughn speaks of "an area of increased hardness at a depth just

below the surface." We have observed, on 1-inch rounds, a *slight* rise beneath the surface after a quench and 900 degrees Fahr. draw. This may be a purely physical "edge effect" in some instances, due to having the Rockwell readings too near the edge. By filing to the depths of the rings showing the increase it has been possible to check this effect. Such peculiarities seem to be of two types; the "surface" and "sub-surface" depressions. The extent of these depressions is *very slight* on the samples we have studied, never exceeding 1.0 to 1.5 Rockwell points at about 30 Rockwell "C." The sensitivity of the readings taken in this neighborhood and the possible edge effect (Rockwell "C" 30 impression has a diameter of almost $\frac{1}{32}$") should be kept in mind. We have never observed this effect on an as-quenched round.

The authors believe that as an indication of hardness penetration the empirical factor suggested is useful. We included our belief, however, that "it is not to be expected that hardenability can be indicated accurately by any simple formula covering a wide range of composition." It should again be pointed out that the variations encountered throughout an entire heat generally exceed the variations observed (±3 Rockwell Inches Area) in fine-grained steels with a factor of 800.

With reference to the suggestion by Messrs. Bain and Davenport that the area under the hardness curve is really the average hardness across the specimen, we deliberately avoided referring to this value as average hardness because of the confusion which would be likely to result. The value is the average hardness across a diameter of a 1-inch specimen, but is far from being the average hardness with respect to the area or volume of the specimen. Furthermore, the area under the curve is numerically equal to the average hardness across a diameter only in the case of a 1-inch diameter specimen. While it is true that we are suggesting the use of the 1-inch specimen as a standard for carbon steels, it is felt that area values for specimens of other diameter will also be useful, especially in the case of alloy steels.

Messrs. Bain and Davenport feel that a larger number of readings is desirable. This would be warranted if the present number did not give the accuracy desired for our test. The accuracy of any test is more or less proportional to the number of readings taken; the number is here limited only by the size of the specimen. Mr. Jameson has illustrated that even half the number of readings we used is sufficient for a practical application.

There is no doubt that segregation can and does cause the effect we have noted in Fig. 8. We are in agreement that this is the better explanation. The only possible way in which the hardness might be slightly higher (from cooling effects) would be displacement of center cooling by more rapid cooling of one bar side. We have omitted that part of the sentence.

Such devices as are described by Mr. Jameson and by Messrs. Bain and Davenport should be helpful in shortening the time necessary for testing for those who do enough testing to justify the cost of a special device. For those who do not have a cut-off machine Bain and Davenport's manner of halving should be useful. The staggering of Rockwell readings is a good suggestion, not only because of possible hardness difference through the piece, but more perhaps because the Rockwell impressions in the softer center area may be too near one another in which case some accuracy may be sacrificed.

In our experience we do not believe that the average reading would be measurably affected by omitting readings obviously abnormal. Incidentally, our mention of these omitted readings referred only to surface readings where decarburization and scale effects cause low values which really should not be considered. Even if a true low hardness area were encountered it could not be any more truly described by a hardenability curve where the soft readings were averaged than by one from which they were omitted. The proper method would be to plot the maximum hardness by omitting soft readings, as we have done, and designating separately the soft area encountered.

Messrs. Bain and Davenport have asked whether we have any explanation for the high hardness obtained at the surface of 3-inch diameter rounds of S.A.E. 1035 and 1045. In connection with the same observations, Mr. Mayo has commented that the critical cooling rate was never exceeded, even at the surface, in sizes over 1 inch in diameter in the case of Dr. Grossmann's S.A.E. 1045 steel. As a matter of fact, examination of Grossmann's curves will show that Grossmann obtained a surface hardness less than 60 Rockwell "C" even at ½-inch diameter. In spite of this, he shows a hardness of about 33 at the center of a 1-inch diameter specimen—which is about the same value we obtained in the instance of the 0.37 carbon steel. Nevertheless, our 0.37 per cent carbon steel shows substantially maximum hardness at the surface of 3-inch diameter bars, whereas Grossmann's S.A.E. 1045 showed only about 36 Rockwell "C" at the surface of a 3-inch diameter bar. It would appear that there must have been a considerable difference in heating or quenching practice in Grossmann's experiments. The high hardness values which we obtained are not due to residual alloys; chromium was 0.04 per cent in the S.A.E. 1035 steel and 0.02 per cent in the S.A.E. 1045 steel. Mr. Mayo's observations on the depth of hardening of large sizes are very interesting and perhaps directly applicable; the fact that he obtains a straight line appears to uphold the uniformity of our quenching technique if his assumptions are correct.

With reference to Mr. Mayo's view that the test is not "quantitative" in the full sense of the word we feel that the test is quantitative in the sense in which it is used. The difference between qualitative and quantitative when referring to hardenability lies chiefly in interpretation; this test permits a quantitative interpretation on a standard basis. It is, of course, true that differences in mechanical treatment, quenching technique and such details may affect results but *no test* can be quantitative unless standard conditions are established. The application of the standard test to a specific problem requires establishing limits; once those limits are established the standard test can then be used to rate, quantitatively, the suitability of different heats. The reproducibility we obtained, and that obtained by Mr. Jameson, indicates that the test *can* be standardized *and* quantitative.

The length of the specimen can, as Mr. Mayo mentions, be shorter in case sufficient material is not available. We used a 4-inch length because it eliminated all tong effect and was convenient to handle.

Generally speaking the quenching temperatures we used were 50 degrees Fahr. above the Ac_3 point. On our "standard" bar of S.A.E. 1045 steel, fine grain, no significant difference was observed in quenching over the range 1450 to 1550 degrees Fahr. The manner of rating the grain size of the tests

charted in Fig. 7 is described in the paper; a careful reading of this paragraph will bring this out. In general it was observed that the normalized grain size (normalized at the quenching temperature) was somewhat finer than that rated at 1700 degrees Fahr. by the McQuaid-Ehn test, that is, the whole scale shifted. Those instances where the grain size was actually intermediate at the quenching temperature although coarse at 1700 degrees Fahr. are indicated in Fig. 7.

In closing, the authors feel that the discussion evoked by this paper demonstrates clearly the interest in and need for information of this type. We hope that this work may be considered a step forward and that the work of subsequent investigation will continue to lessen the confusion which has so long been prevalent in the field of commercial hardenability.

PRECIPITATION HARDENING OF COBALT STEEL: A NEW TOOL MATERIAL

By R. H. Harrington

Abstract

An alloy of 36 per cent cobalt, 8 per cent molybdenum, 6 per cent chromium, 1 per cent carbon, 0.4 per cent vanadium, balance iron, may be forged, cut, machined, welded, and brazed. The alloy may then be precipitation hardened[1] to a Rockwell A hardness of 88, about 72 Rockwell C. It gives promise of being a useful tool material in a class between high speed steel and the sintered carbides.

Introduction

An alloy of 36 per cent cobalt, 5 per cent molybdenum, 5.4 per cent chromium, 1 per cent carbon, balance iron has found use in some types of instrument magnets. It was claimed that the field at the pole faces was concentrated somewhat by heating and softening the pole tips with a very small gas torch. Curiosity led to Rockwell hardness tests and the discovery that the hardness at the tips had been increased from about 62 to 64 C of the normally hardened magnet to 68 to 69 C for the reheated pole tips, clearly a case of precipitation hardening.

Five standard magnetic test bars of this analysis were given various pre-quench treatments and were then oil-quenched from 950 degrees Cent. (1740 degrees Fahr.). Their magnetic properties, resistivities, and Rockwell C hardness values were measured. All bars were then aged six hours at 450 degrees Cent. (840 degrees Fahr.) and these measurements repeated. The results are given in Table I. The hardness was increased about four points and the changes in the other properties offered proof of the occurrence of precipitation hardening.

[1]U. S. Patent 2,043,533.

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. The author, R. H. Harrington, is Research Metallurgist, General Electric Company, Schenectady, N. Y. Manuscript received June 2, 1937.

Hardness Tests

In order to save the diamond point during subsequent tests, the Rockwell A test was mostly used. For comparison with the Rockwell C hardness of various high speed steels, these Rockwell A values

Table I

Sample	Max. β	βr	H_c	B_o	βH max.	Microhms/cm³	Treatment
144-1	11400	6600	230	6320	501,000	89.4	Normalized at 1150°C and oil quenched at 950°C
-2	12000	6900	230	6190	567,000	89.7	Normalized at 1150°C and oil quenched at 950°C
-3	13550	8550	230	8190	755,000	83.6	Oil quenched at 950°C
-4	13350	8850	230	8080	841,000	82.3	Oil quenched at 950°C
-5	11100	6600	230	6400	527,000	83.0	Normalized at 1150°C Oil quenched at 950°C
144-1	15400	8700	140	8280	474,000	59.6	Age hardened 6 hrs. at 450°C. Air-cooled
-2	15400	8700	150	8200	500,000	59.3	Age hardened 6 hrs. at 450°C. Air-cooled
-3	17100	10700	120	9900	495,000	52.0	Age hardened 6 hrs. at 450°C. Air-cooled
-4	17000	10600	115	9860	505,000	51.8	Age hardened 6 hrs. at 450°C. Air-cooled
-5	14850	8850	125	8450	445,000	57.3	Age hardened 6 hrs. at 450°C. Air-cooled

Rockwell C Hardness

Bars	Before Age Hardening	After Age Hardening
144-1	60	64
-2	59	63
-3	66	68
-4	65	68.5
-5	59	64

were transferred to Rockwell C values according to Table II. This table gives the normal transfer values up to Rockwell C 65 and the extrapolated values up to C 75. A few actual Rockwell C tests on samples giving A 88 resulted in C values of 72-73. Microscopic measurement of the diameter of the depressions led to "calculated Brinell" hardness values in the range of 1300 to 1500, so it is felt that the table is reasonably accurate.

Development of Composition

Six different analyses were made up in 100-pound ingots melted in and cast from high frequency coreless induction furnaces. To all melts additions of 0.4 per cent manganese and 0.4 per cent silicon were made to care for sulphur and oxygen. Thorough precipitation hardening studies were made of each alloy in the cast and forged

conditions. It is possible to develop the maximum hardness characteristic of each alloy in both the forged and cast conditions. The alloys were then compared on the basis of analysis and maximum hardness developed. Table III gives these results.

Table II

Rockwell C	Rockwell A	Brinell Hardness
75	89.5	...
74	89.0	...
73	88.5	...
72	88.0	...
71	87.5	...
70	87.0	...
69	86.5	...
68	86.0	...
67	85.5	...
66	85.0	...
65	84.0	690
64	83.5	673
63	83.0	658
62	82.5	645
61	82.0	628
60	81.5	614
59	81.0	600
58	80.5	587
57	80.0	573
56	79.5	560
55	79.0	547
54	78.5	534

Extrapolated Rockwell C and A Hardness Values.

Alloy No. 2 gave the greatest hardness value in this series and is characterized by high carbon, high cobalt, and high molybdenum. Fractures of all alloys, except No. 4, were exceedingly fine-grained

Table III

Alloy No.	Per Cent Carbon	Per Cent Chromium	Per Cent Cobalt	Per Cent Molybdenum	Per Cent Vanadium	C Max. Hard.
A (magnet)	1.00	5.4	36.3	4.9	..	68
1	1.20	7.27	36.4	5.2	..	69
2	1.14	6.71	35.4	8.5	0.4	72
3	0.75	5.10	32.6	6.1	0.4	69
4	0.58	6.70	33.0	5.03	0.4	40
5	0.87	6.37	21.9	9.50	0.4	65

with the fineness of grain somewhat enhanced by the small addition of vanadium. The lower hardness of alloy No. 4 was apparently due to the lower carbon content. Comparison of alloys 3 and 5 shows that the higher cobalt content is necessary to achieve the higher hardness.

Since hardness of itself is not directly indicative of actual cutting

tool performance, a standard tool test was applied to tools tipped with alloys A, 1, 2, 3 and 5. The tool shanks were made of 3 per cent nickel steel, ½ inch x 1⅛ inches in cross section. The tip-pieces of the alloys were copper-brazed to the shanks and the tools were then given the precipitation hardening treatments to develop maximum hardness. The heat treatment consisted of a 1-hour heat at 950 degrees Cent. (1740 degrees Fahr.), oil quench, and a reheat of five hours at 500 degrees Cent. (930 degrees Fahr.) followed by air cooling. The noses were ground to the standard shape for a high speed steel tool of the 18-4-1 variety which was included in the cutting tests for comparison. A 0.35 per cent carbon, 3 per cent nickel steel log with a Brinell of 195 was used for cutting stock and was about 10 inches in diameter. The conditions were: ¼ inch depth of cut, 20 mil feed, and a speed of 70 feet per minute. The tools are listed with their resulting time runs, averages for three tools of each alloy.

High speed steel, 18-4-1 type	6½ min.	Failure
Alloy A	12½ min.	Failure
Alloy 1	16½ min.	Failure
Alloy 2	30 min.	*No* failure
Alloy 3	30 min.	*No* failure
Alloy 5	25 min.	Failure

In order to differentiate between the outstanding tools of alloys 2 and 3, these were further tested without regrinding. Cutting conditions were: ¼ inch depth of cut, 25 mil feed, and a speed of 80 feet per minute. Tools of alloy No. 2 ran an additional 4½ minutes to failure while No. 3 tools failed after an additional 1½ minutes under the changed conditions. As the result of these tool tests, alloy No. 2 was chosen as the best of the series.

Precipitation Hardening of Alloy No. 2

For tools over one-half inch square in cross section, the most economical procedure will usually be to copper braze tips on to a steel shank. This will entail heating the material in excess of 1100 degrees Cent. (2010 degrees Fahr.). To soften the material for machining, a 750 degrees Cent. (1380 degrees Fahr.) anneal may be used. Consequently the hardening study includes the effects of these pre-hardening heat treatments. Since most tool bits will be cut from forged stock, these data were obtained from samples of 1-inch square bar forged from 4½ inches square ingot.

Different samples were given the following treatments and tested for hardness following various periods of time at successively higher drawing temperatures. The hardness data are plotted in Figs. 1 and 2.

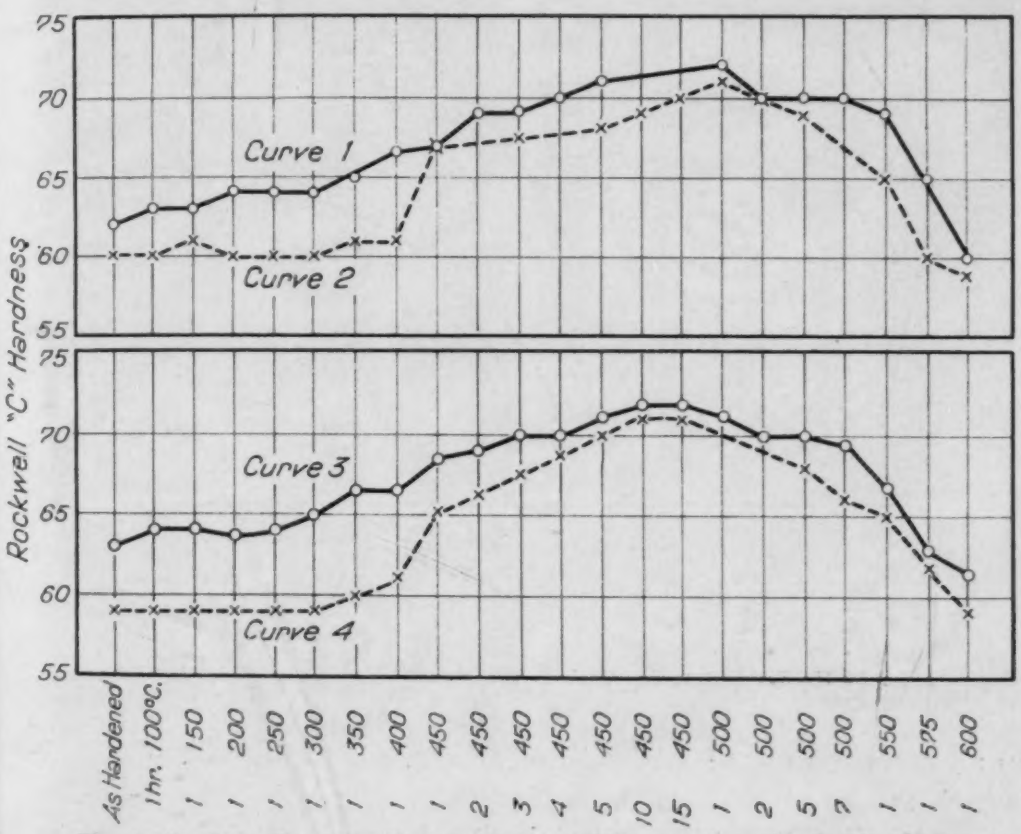


Fig. 1—Hardness Data for Various Periods of Time at Successively Higher Drawing Periods.

Pre-hardening heat treatments:

Curve 1. One hour at 950 degrees Cent. (1740 degrees Fahr.) and quenched in oil.

Curve 2. Normalized one-half hour at 1150 degrees Cent. (2100 degrees Fahr.); one hour at 950 degrees Cent. (1740 degrees Fahr.) and quenched in oil.

Curve 3. Annealed one hour at 750 degrees Cent. (1380 degrees Fahr.); one hour at 950 degrees Cent. (1740 degrees Fahr.) and quenched in oil.

Curve 4. Normalized at 1150 degrees Cent. (2100 degrees Fahr); annealed at 750 degrees Cent. (1380 degrees Fahr.); one hour at 950 degrees Cent. (1740 degrees Fahr.) and quenched in oil.

Curve 5. Oil-quenched after one-half hour at 1150 degrees Cent. (2100 degrees Fahr.).

From the curves one can see that normalizing or copper-brazing cycles previous to hardening result in a maximum precipitation hardness about one point, Rockwell C, lower than the maxima obtained for the steel in the "as-forged" or "forged and annealed" conditions.

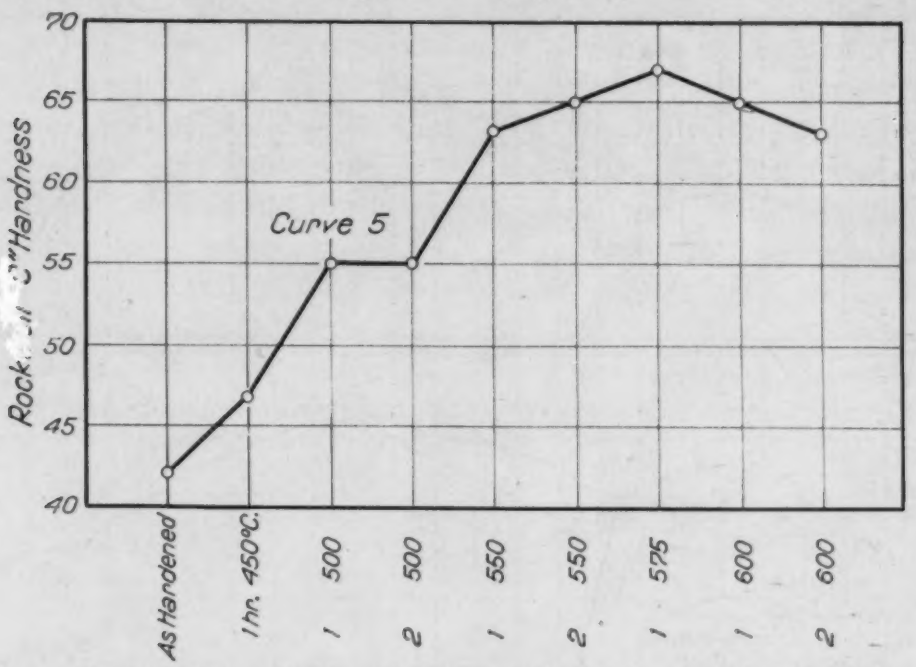


Fig. 2—Hardness Data for Various Periods of Time at Successively Higher Drawing Periods.

In all cases the use of a 950 degrees Cent. (1740 degrees Fahr.) oil quench treatment permits the achievement of precipitation hardness values of 71 to 72. The precipitation hardening reheat after the quench may vary from five hours at 450 degrees Cent. (840 degrees Fahr.) to five hours at 500 degrees Cent. (930 degrees Fahr.) followed by air cooling and dependent somewhat on the previous treatment of the piece. Even an oil quench from 1150 degrees Cent. (2100 degrees Fahr.) yields a surprising degree of precipitation hardening from 42 Rockwell C after the quench to a maximum of 67 after a draw at 575 degrees Cent. (1070 degrees Fahr.).

Structures

The photomicrographs at magnifications of X 200 and X 1500 show the structures developed in forged stock by the following successive heat treatments:

Figs. 3 and 4. 750 degrees Cent. (1380 degrees Fahr.) anneal. One hour at 750 degrees Cent. (1380 degrees Fahr.) and furnace cooled.

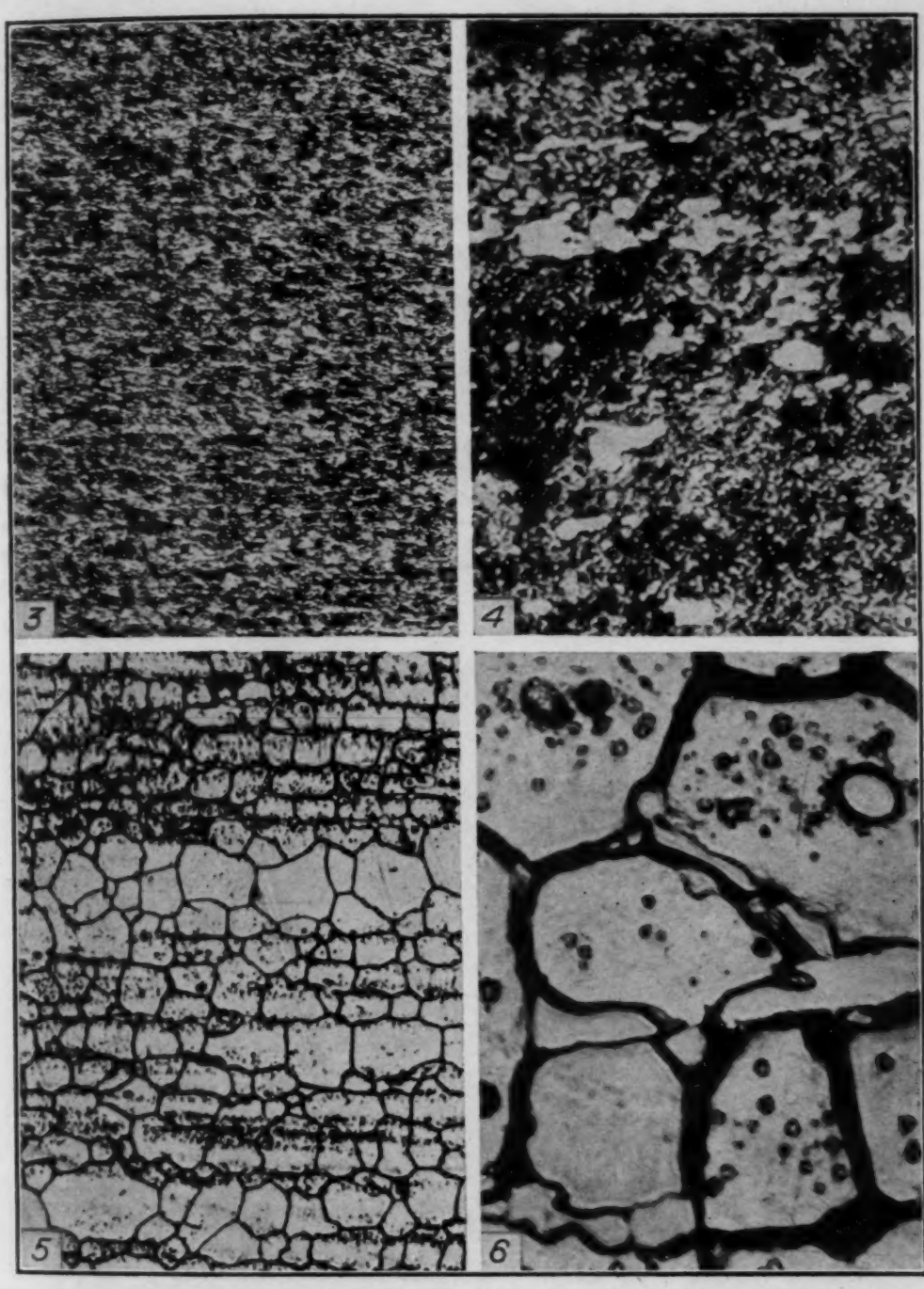


Fig. 3—One Hour at 750 Degrees Cent. (1380 Degrees Fahr.) Furnace-Cooled. × 200.

Fig. 4—Same as Fig. 3. × 1500.

Fig. 5—One Hour at 1150 Degrees Cent. (2100 Degrees Fahr.) Air-Cooled. × 200. Previous Treatment: 1 Hour 750 Degrees Cent. (1380 Degrees Fahr.) and Furnace-Cooled.

Fig. 6—Same as Fig. 5. × 1500.

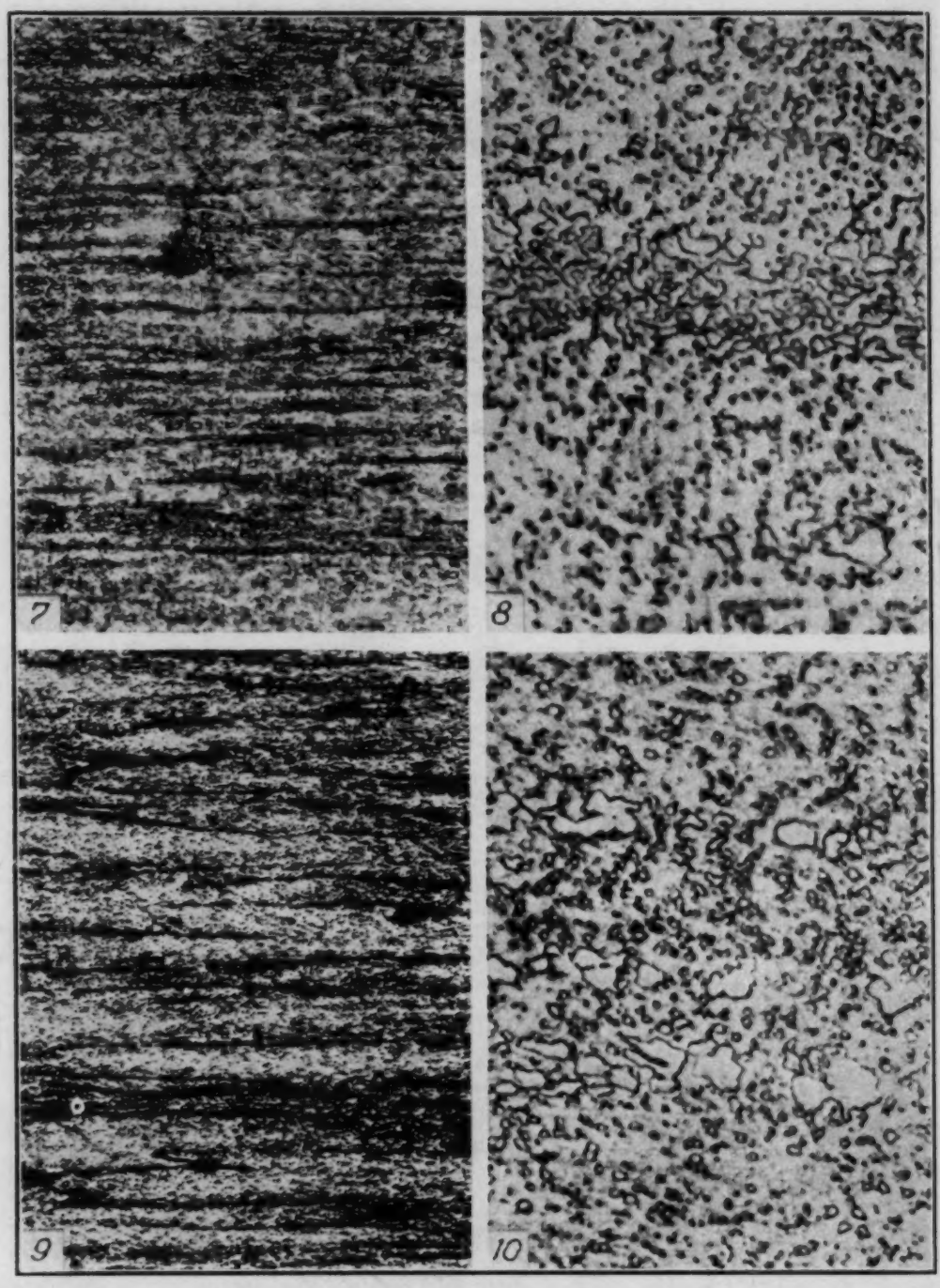


Fig. 7—One Hour at 950 Degrees Cent. (1740 Degrees Fahr.) Quenched in Oil. × 200. Previous Treatment: 1 Hour 750 Degrees Cent. (1380 Degrees Fahr.) Furnace-Cooled. 1 Hour at 1150 Degrees Cent. (2100 Degrees Fahr.). Cooled in Air.

Fig. 8—Same as Fig. 7. × 1500.

Fig. 9—One Hour at 950 Degrees Cent. (1740 Degrees Fahr.). Quenched in Oil. Reheated 5 Hours at 500 Degrees Cent. (930 Degrees Fahr.) and Air-Cooled. × 200. Previous Treatment: 1 Hour 750 Degrees Cent. (1380 Degrees Fahr.). Furnace-Cooled 1 Hour 1150 Degrees Cent. (2100 Degrees Fahr.). Air-Cooled.

Fig. 10—Same as Fig. 9. × 1500

Figs. 5 and 6. Normalized at 1150 degrees Cent. (2100 degrees Fahr.). One hour at 1150 degrees Cent. (2100 degrees Fahr.) and air-cooled.

Figs. 7 and 8. One hour at 950 degrees Cent. (1740 degrees Fahr.), then quenched in oil.

Figs. 9 and 10. One hour at 950 degrees Cent. (1740 degrees Fahr.), oil-quenched, then five hours at 500 degrees Cent. (930 degrees Fahr.) and air-cooled.

Fig. 6 indicates that there may be two hardening phases, one that etches white and the other dark with Nital. Comparing Figs. 8 and 10, it would seem that the white phase precipitates during the quenching treatment giving a hardness of 60–64 Rockwell C while the dark appearing phase precipitates during the "draw" at 450–500 degrees Cent. (840–930 degrees Fahr.) and giving a precipitation hardness of 70–72 Rockwell C. (88 Rockwell A).

Preparation of a Tool

(1) *Melting Practice.* Conditions such as starting with a cold or a warm furnace, type of mold, type of melting furnace, will, of course, alter somewhat the amounts of additions and the melting procedure. For a melt starting with a cold coreless induction furnace, a total charge of 140 lbs. cast into a 4 x 4 inch preheated ingot mold, the following table lists the materials charged and the resulting analysis:

Per Cent of Element Charged	Material Form	Resulting Analysis Per Cent
37.6 Cobalt	rondelles	36.4 Cobalt
5.6 Chromium	(70 Chromium—30 Iron) ferrochromium	5.52 Chromium
8.8 Molybdenum	Molybdenum scrap	8.50 Molybdenum
0.58 Vanadium	(43 Vanadium—57 Iron) ferrovanadium	0.43 Vanadium
1.1 Carbon	graphite	0.98 Carbon
Balance Iron		Balance Iron

There are two methods for adding the carbon:

(a) Melt the iron and cobalt. Add half the additions of molybdenum, and ferrochromium. Cut off the power. Add the carbon as graphite pushed to bottom of melt with an iron rod and add rest of molybdenum and ferrochromium as melt freezes in the furnace after cutting off the power. Remelt. Add 0.4 manganese and 0.3 silicon and the ferrovanadium. Pour.

(b) Melt the whole charge under illuminating gas. Add 0.85

per cent carbon as graphite plunged to bottom of melt with an iron rod. Kill the melt with about 0.2 per cent aluminum and pour.

(2) *Forging Practice.* The ingot is charged into a cold furnace and heated with the furnace to a temperature of 1150 degrees Cent. (2100 degrees Fahr.). The ingot is held at temperature for two to four hours. This temperature is quite critical as the first forging is ineffective at lower temperatures and the ingot will become mushy and spoiled at 1200 degrees Cent. (2190 degrees Fahr.). The ingot at 1150 degrees Cent. (2100 degrees Fahr.) is struck very lightly and rapidly on all four sides, effecting about ⅛ inch reduction on all sides and then it is soaked for one-half hour at 1150 degrees Cent. (2100 degrees Fahr.). Following this initial forging, the blows can be increased in severity and forging can, after the third reduction, be carried on in the range from 1150 degrees Cent. (2100 degrees Fahr.) down to 900 degrees Cent. (1650 degrees Fahr.) and the alloy forges readily to the finished size. For tool tip stock the ingot is usually forged into bars of one square inch cross section. Following the last forging the bar is air-cooled.

(3) *Cutting.* The tip stock can be cut with a saw but cutting with a Radiac wheel is easier and more rapid.

(4) *Shanks.* Shanks may be of carbon steel but are preferably made of 3 per cent nickel steel to withstand the heat cycle attending the copper brazing of tip to shank. Tip sizes for any given tool are similar to those for tips of sintered carbide. The tip seat is milled into the shank.

(5) *Tipping the Tool.* The tip may be applied to the shank by (1), copper brazing in a furnace; (2), copper brazing by resistance heating of tool nose and alloy tip; (3), arc-welding.

(6) *Rough Shaping of Tool Nose.* The tool nose is rough ground using the same grinding practice as with high speed steel. Usually better cutting is obtained with the tip face angles designed for carbide-tipped tools rather than those for high speed steel.

(7) *First Heat Treatment.* The whole tool is heated one hour at 950 degrees Cent. (1740 degrees Fahr.) and then quenched in oil.

(8) *Finish Grinding.* The tool is finish ground to size and final face angles using high speed steel grinding practice.

(9) *Precipitation Hardening Treatment.* The tool is then heated for five to ten hours at 450 degrees Cent. or one to five hours at 500 degrees Cent. (930 degrees Fahr.) and air-cooled. Practice will determine the better heat treatment for the particular cutting application.

(10) *Cleanup Grind.* A very light cleanup grind will remove the thin film of oxidized surface from the final heat treatment and will develop an exceedingly keen cutting edge. The tool is then ready for use.

Some Tool Tests and Applications

A few tool tests and applications are reported here for the sole purpose of making practical comparisons with high speed steel.

(1) Tools were used to machine the outside scaled surface of tubes made from 0.08 per cent carbon drawn seamless steel tubing. Conditions: 20 mil feed, $\frac{1}{16}$ inch depth of cut, 225 feet per minute speed. The alloy tipped tool finished 40 tubes between grinds as compared to 15 tubes for high speed steel and 75 tubes for a sintered carbide tool between grinds.

(2) Machined 0.80 per cent carbon steel. Conditions: $\frac{1}{32}$ inch feed, $\frac{3}{16}$ inch depth of cut, speed of 74 feet per minute. Diameter of stock was 1½ inches. After machining 5 feet length of stock the tool edge was still good, while high speed steel tool needed regrinding after 2 feet of cutting.

(3) The face of a 42-inch diameter disk of 98.5 copper, 1.5 tin was cut at speeds from 30 feet per minute at the center to 80 feet at the circumference. The feed was ⅛ inch and depth of cut, ½ inch. The life of the tool between grinds was 18 hours compared to 6 hours for high speed steel tool.

(4) Cobalt magnet steel is very tough to machine. Alloy tipped tools were used to machine ¾-inch diameter rods from 1-inch square cast ingots in one cut. Conditions: 8 mils feed, ⅛ to $\frac{3}{16}$ inch depth of cut, 30 to 40 feet per minute speed. The edge of a high speed steel tool was dulled after cutting 1 inch length of stock, while the alloy tipped tool was in perfect condition after machining six one foot lengths.

(5) Alloy tipped tools are economically used to machine the brush surface of assembled commutators, mica separators between the copper segments.

(6) Swaged tungsten rod of 1 inch diameter was machined with an alloy tipped tool. Conditions: 10 mil feed, ⅛ inch depth of cut, 30 feet per minute speed.

(7) Under finish and semi-finish cutting conditions, alloy tipped tools are far superior to high speed steel, giving much longer life at

higher cutting speeds and leaving a better machined surface on the stock.

(8) Six 3/8-inch square bits of the alloy were mounted in the periphery of a 6-inch disk of steel, the bits being perpendicular to the disk face. The steel disk was mounted directly on the shaft of an 1800 revolutions per minute motor. A variable depth of cut of 3 to 10 mils was taken, the feed was 10 mils, and the speed about 2900 feet per minute. The material machined was Sabeco metal and the finished surface was so good that the usual emery cloth finish was omitted. The life was about ten times the life of high speed steel bits.

(9) Bakelite is very successfully machined with these alloy tipped tools.

While there are as yet no real results available from production usage, there is ample evidence that these alloy tipped tools by performance may be classified as intermediate to high speed steel tools and those tipped with sintered carbide.

Conclusions

(1) An alloy of 36 per cent cobalt, 8 per cent molybdenum, 6 per cent chromium, 1 per cent carbon, 0.4 per cent vanadium, balance iron, may be precipitation hardened to a Rockwell C hardness of 71–72 (Rockwell A 88).

(2) The precipitation hardening heat treatment consists of one hour at 950 degrees Cent. (1740 degrees Fahr.), quench in oil, and reheat about five hours at 450–500 degrees Cent. (840–930 degrees Fahr.), followed by air cooling.

(3) The alloy may be forged, swaged, rolled and drawn at temperatures of about 1150–1100 degrees Cent. (2100–2010 degrees Fahr.).

(4) The alloy is machinable.

(5) Tool tests indicate that, as a tool material, the alloy may be classified as intermediate to high speed steel and sintered carbide materials.

(6) The copper brazing cycle for fixing the alloy tips to shanks of 3 per cent nickel steel is the normalizing treatment for the alloy.

(7) Tests indicate outstanding performance for the alloy tipped tools for the finish and semi-finish machining of copper, brass, steel, cast iron, bakelite, etc.

(8) These alloy tools are readily ground to an exceedingly

keen edge, the fine cutting performance probably being due to this keen edge and the superior hardness developed by heat treatment.

ACKNOWLEDGMENTS

The writer here expresses his appreciation for the photomicrographs taken by Mr. L. L. Wyman.

DISCUSSION

Written Discussion: By W. P. Sykes, General Electric Co., Cleveland.

The alloys described by Dr. Harrington appear to illustrate nicely certain characteristics common to iron base alloys which owe their precipitation hardening properties in part to the presence of carbon. Without knowledge of the phasial equilibrium relationships existing in these compositions, it is of course impossible to be sure of the structural changes which accompany the changes in hardenss. It would seem, however, that at 950 degrees Cent. (1740 degrees Fahr.) we might expect to find a gamma solid solution partially saturated with carbon, chromium and molybdenum, which during the quench changes to the alpha form. This decomposition is accompanied by the precipitation of carbides and results in a structure of the martensitic type with a hardness of about C 60. Upon reheating in the range of 300 to 500 degrees Cent. (570 to 930 degrees Fahr.), further precipitation of carbides occurs within the quenched structure increasing the hardness to a maximum of C 72 after 10 to 15 hours at 450 degrees Cent. (840 degrees Fahr.), as shown in Fig. 1.

It is of interest to observe, however, the rapid decrease in hardness as the aging or "tempering" temperature is raised to 600 degrees Cent. (1110 degrees Fahr.). After 1 hour at 600 degrees Cent., the hardness is below that of the quenched alloy. This tendency to over-age rapidly at temperatures above 500 degrees Cent. (930 degrees Fahr.) seems to generally mark those alloys in which the precipitating phase is a carbide and especially when some precipitation occurs during the initial cooling or quenching.

By heating to 1150 degrees Cent. (2100 degrees Fahr.) before quenching, the initial hardness is lowered to about C 40 as we see from Fig. 2. This might result from (1) the retention of a delta (or high temperature alpha) solid solution or (2) a more completely saturated gamma solution which transforms to alpha without the precipitation of a second phase. After quenching from 1150 degrees Cent. (2100 degrees Fahr.) the hardness which is developed upon reheating reaches a maximum at 575 degrees Cent (1065 degrees Fahr.) instead of at 450 degrees Cent. (840 degrees Fahr.) as was the case when quenched from 950 degrees Cent. (1740 degrees Fahr.). While this maximum is about C 67 instead of C 72 as in the former case, it should be observed that the hardness of the alloy as quenched from 1150 degrees Cent. (2100 degrees Fahr.) resists the 600 degrees Cent. (1110 degrees Fahr.)

aging treatment more successfully than if never heated above 950 degrees Cent. (1740 degrees Fahr.) before the quench. Generally speaking, the performance of the alloys as depicted in Fig. 1 resembles that of high speed steel in contrast to the time-hardness curve of Fig. 2, which suggests rather the type belonging to carbon-free iron base alloys containing some 30 per cent cobalt and appreciable amounts of tungsten or molybdenum.

As Dr. Harrington has remarked, the important part played by carbon in the hardening of these alloys is unmistakably revealed in Table III by the relatively low hardness of alloy No. 4 which contains but 0.58 per cent carbon, as compared to the 1.2 per cent carbon content of alloy No. 1. Aside from this difference, the analyses of these alloys are nearly identical.

Oral Discussion

J. P. GILL:[1] The use of precipitation hardening materials for cutting alloys has not been very generally accepted, and there appears to be two definite objections. The first is machinability of such alloys. Most of these alloys seem to be rather difficult to machine, particularly into fine-edge tools. The second objection seems to be that most of these alloys are extremely brittle at the maximum hardness at which hardness they are generally used. I would be interested in knowing if Mr. Harrington has any data regarding either machinability of this material or its toughness at maximum hardness. In reference to the effect of carbon, many people do not seem to recognize that in the cobalt-chromium alloys of the stellite type, although not originally considered important, it is generally accepted today that the carbon content in these alloys is of great influence on their properties and performance.

DR. HARRINGTON: In answer to Mr. Gill about the machining of the alloy, it machines about as readily as high speed steels in the unhardened condition. To machine the softened alloy we use tools tipped with carbide or with the new alloy. In the finally hardened condition, it is a very easily ground material. The final grinding of the tool edge is much more readily effected than with even a high speed steel. Our material is, I believe, more brittle than high speed steel, although I do not have any quantitative figures to show that. I am quite sure it is somewhat more brittle, though not as brittle as the carbides.

I greatly appreciate the discussion of Mr. Sykes. He has raised some questions which I felt I did not know enough about to discuss at this time. I should like to quote from his discussion, "This decomposition is accompanied by the precipitation of carbides and results in a structure of the martensitic type with a hardness of about C 60." It is a curious thing that with these compositions we have as yet never noted a structure comparable to that of the martensite, and in general I do not beleieve that such compositions are, strictly speaking, steels. They are better viewed as ferrous alloys, and that, I believe, is the way Mr. Sykes has always viewed such alloys in the work which he has treated so thoroughly in previous publications.

The second point which I would make is this, quoting from Mr. Sykes' discussion, "Generally speaking the performance of the alloys as depicted in

[1]Chief metallurgist, Vanadium-Alloys Steel Co., Latrobe, Pa.

Fig. 1 resembles that of high speed steel in contrast to the time-hardness curve of Fig. 2, which suggests rather the type belonging to carbon-free iron base alloys containing some 30 per cent cobalt and appreciable amounts of tungsten or molybdenum." We do not have sufficient data to prove the point, but I have felt that the quenched hardness was due primarily to carbides, and the hardness from the drawing temperatures of 450 to 575 degrees Cent. was probably largely due to some other agent, such as a compound of cobalt and molybdenum. I am wondering if these two suggestions of Mr. Sykes have not more or less upheld that viewpoint.

THE RUPTURE STRENGTH OF STEELS AT ELEVATED TEMPERATURES

By A. E. White, C. L. Clark and R. L. Wilson

Abstract

This paper presents results obtained from long time rupture tests on eight steels at temperatures from 1000 to 1500 degrees Fahr. The time for fracture was varied from a few minutes to several thousand hours. A definite relationship was found to exist for each analysis between stress and fracture time.

The chief merits of the rupture tests were found to be that (1) they serve as a suitable basis for the design of high temperature apparatus in which some deformation of the parts is permissible, and (2) they afford the best means available for determining the ductile properties of steels under the combined action of stress, time and heating.

THE necessity of having a measure for the strength of steels at elevated temperatures attracted the attention of investigators in this field long ago. It was natural that the earliest tests should resemble the tensile test used for determining the strength of steels at ordinary temperatures. Eventually the idea of a long time tensile rupture test was developed, but before the possibilities of the test could be established, interest had shifted to the creep test in which the rate of flow of the metal under stress was emphasized. For a number of years now the creep strength has been generally preferred to the long time rupture test in the design of equipment for high temperature service.

With the increased use of creep data came the improvements in apparatus and the standardization of testing procedure that have aided so greatly in systematizing the test and eliminating discrepancies between laboratories. The creep test has been tentatively defined with respect to dimensions of specimen, method of measuring temperature distribution in the furnace, temperature regulation, and

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. Of the authors, A. E. White and C. L. Clark are director and research engineer, respectively, Department of Engineering Research, University of Michigan, Ann Arbor, and R. L. Wilson is metallurgical engineer, Climax Molybdenum Co., Canton, Ohio. Manuscript received June 22, 1937.

minimum duration of testing period for extensometers of certain sensitivity. Nevertheless, inconsistencies are now becoming apparent at least in some steels to indicate that they are changing remarkably in character during the progress of the test.

Ordinarily the creep strength of steels is expressed as the stress producing creep at the rate of one per cent in 100,000 hours or in 10,000 hours based upon the assumption that these rates of creep as observed in tests of approximately 1000 hours' duration would hold for the longer time periods. Some of the data show that extrapolations of this kind are unreliable, especially for creep strength values for one per cent in 10,000 hours. As examples, tests made on electric furnace carbon steel and a low alloy composition at 1000 degrees Fahr. may be cited. In 1000-hour creep tests the carbon steel gave a creep strength of 5750 pounds per square inch for one per cent in 10,000 hours, but in the long time loading the specimen had actually fractured in 13,950 hours under a stress of 6000 pounds per square inch as seen in Fig. 1. Similarly, the low alloy steel had a creep strength of 22,000 pounds per square inch and ruptured after only 6151 hours under a stress of 24,600 pounds per square inch as indicated in Fig. 2. From this it is evident that these steels have failed under conditions where limited deformation would have been predicted from the creep data.

The creep strength values for a rate of creep of one per cent in 100,000 hours have never shown such glaring inconsistencies, although the tests on one alloy steel having a creep strength of 13,000 pounds per square inch in 1000-hour tests at 1000 degrees Fahr. will apparently rupture after 35,000 hours under this same stress, according to a reasonable extension of the rupture strength curve of the material. In general, it seems that the creep strength for a rate of creep of one per cent in 100,000 hours from 1000-hour tests is a fairly reliable strength value, because the time required for the fracture of steels subjected to this stress is very long. On the other hand, the idea that a test started as a creep test should end in the fracture of the specimen was surprising enough to revive interest in the long time tensile rupture tests of the early investigators.

Rupture strength of steels would not appeal to turbine builders, who must make allowances for quite small plastic movements of metal. However, for the construction of various high temperature tubular coils for heaters in oil refineries and for special boiler and superheater tubing the concept of a long time rupture strength would

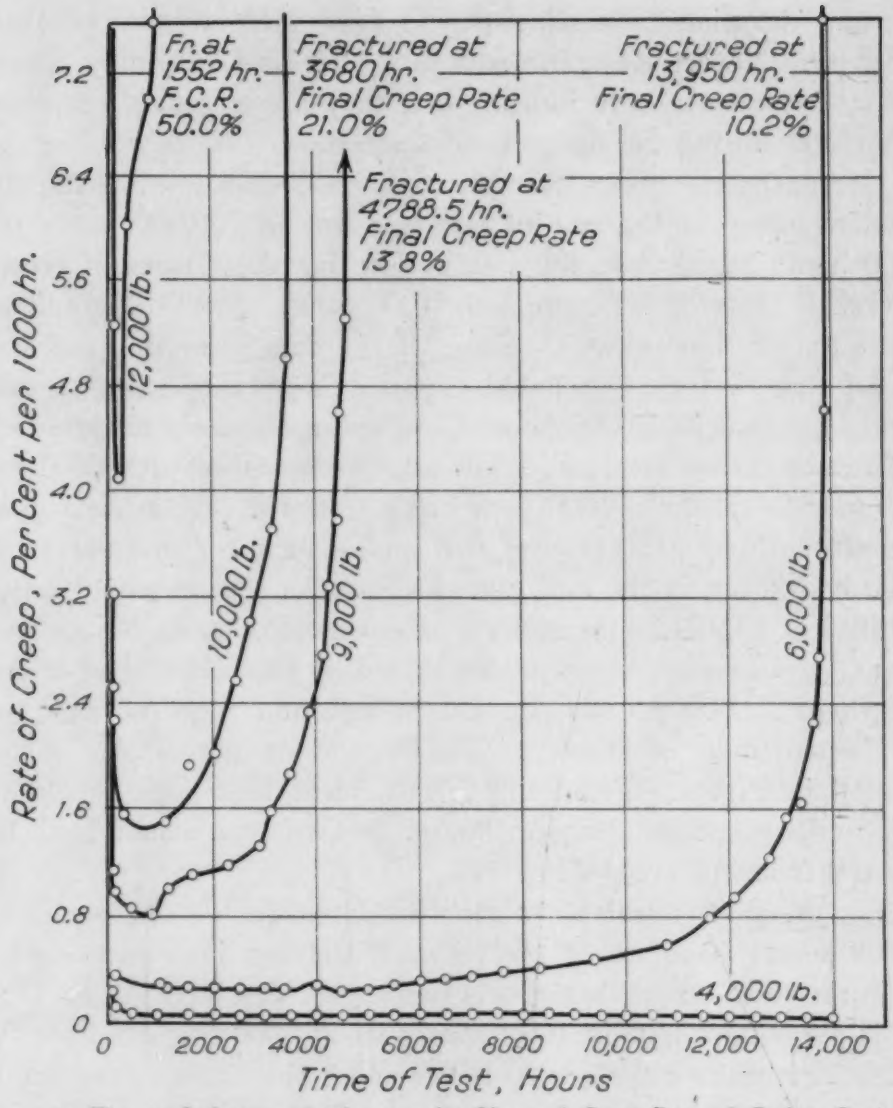


Fig. 1—Influence of Time on the Observed Creep Rate of Carbon Steel at 1000 Degrees Fahr.

prove useful by providing (1) strength data for design purposes and (2) an assessment of the behavior of a steel on long heating under stress.

Procedure

The procedure involved in making the rupture tests and in interpreting the results was described in a paper[1] before the Society last year. The test consists mainly in subjecting a series of specimens of each analysis at each temperature to several different fixed loads and recording the time for fracture. These loads are adjusted so that the

[1] A. E. White, C. L. Clark and R. L. Wilson, "The Fracture of Carbon Steels at Elevated Temperatures," Transactions, American Society for Metals, Vol. 24, 1937, p. 863.

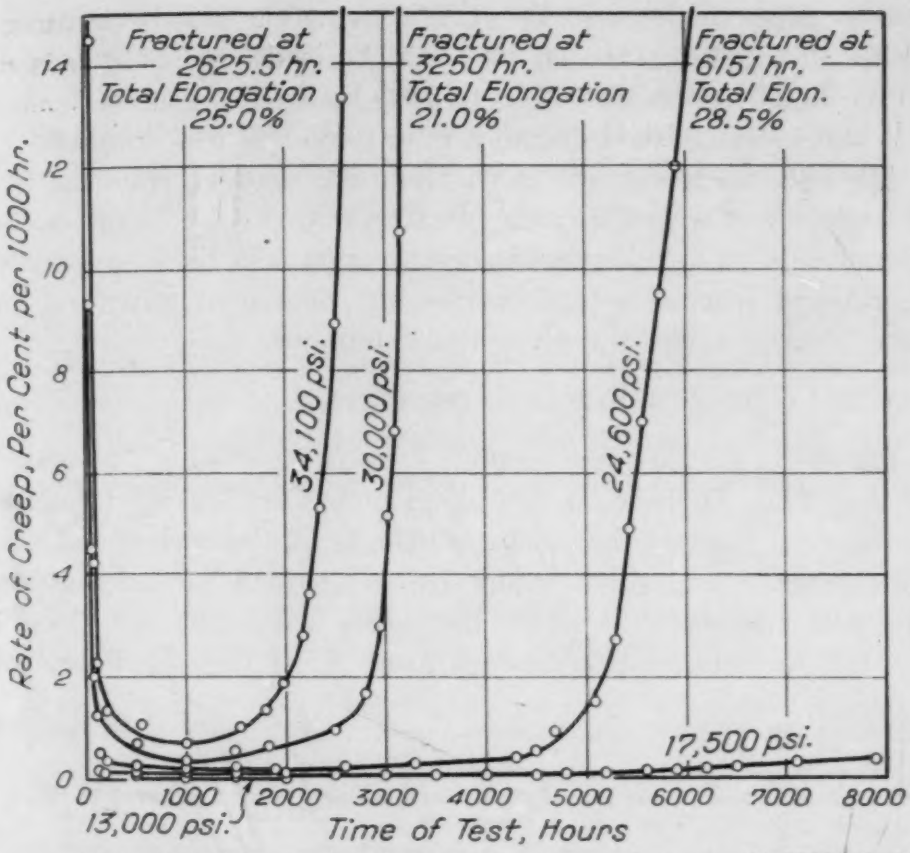


Fig. 2—Influence of Time on the Observed Creep Rate of a Cr-Si-Mo Steel at 1000 Degrees Fahr.

fracture time will vary from a few minutes to several hundred hours. A measurement of the ductility characteristics of the fractured specimens then gives an indication of the influence of time, temperature and stress on this property.

It was further found that a logarithmic plotting of stress and the corresponding fracture time resulted in a straight line relationship provided the steel possessed freedom from oxidation. If the analysis were susceptible to surface or intergranular oxidation, the relationship between stress and fracture time is expressible by another straight line having a different slope.

It follows, therefore, that on the basis of this method the ideal stress-fracture relationship could be obtained from tests of rather short duration. This thus affords a means of determining the relative merits of a large number of analyses in a relatively short time period and, for tests for this purpose, five fracture times covering a total range of 200 to 300 hours have been found to be sufficient.

When complete information is not available with respect to the

surface stability of the steel, or when information with respect to the influence of fracture time on the ductility is desired, it is believed the tests should run at least 2000 to 3000 hours. In general, definite trends will be established during a time period of this duration.

Attempts are also made to correlate the findings from the long time rupture test with the creep characteristics, at the corresponding temperatures. A metallographic investigation was likewise made of the fractured specimens to determine the degree of structural and surface stability under the given test conditions.

Steels Investigated

The steels for this investigation were furnished by The Timken Steel and Tube Division of The Timken Roller Bearing Company. They were all available in the form of hot-rolled 1-inch round bars. Their chemical composition, grain size and Brinell hardness, as well as the heat treatment to which they were subjected, are given in Table I. An annealing treatment from 1550 degrees Fahr. was employed for all of the steels except two. The 18-8 was water-quenched from 2000 degrees Fahr. while the alloy designated as 5-2-3 was normalized from 1800 degrees Fahr.

Table I
Chemical Composition, Grain Size, Brinell Hardness and Heat Treatment of Steels Considered

Designation	Chemical Composition							Grain Size	Brinell Hardness	Heat Treatment Deg. Fahr.
	C	Mn	Si	Cr	Mo	Ti	Ni			
1015 (OH)	0.15	0.46	0.28	....	....	....	....	5-6	111	Ann. 1550
1015 (El)	0.15	0.50	0.23	....	....	....	....	4-5	134	Ann. 1550
Cr-Si-Mo	0.07	0.42	0.72	1.24	0.54	....	....	4-5	123	Ann. 1550
4-6 Cr-Mo	0.10	0.45	0.18	5.09	0.55	....	....	7	131	Ann. 1550
4-6 Cr-Mo-Si	0.10	0.38	1.55	4.83	0.51	....	....	4-6	156	Ann. 1550
4-6 Cr-Mo-Ti	0.10	0.44	0.38	4.98	0.50	0.51	....	4-6	126	Ann. 1550
5-2-3	0.12	0.42	2.24	5.54	2.77	....	....	...	201	Nor. 1800
18-8	0.06	0.50	0.61	17.75	....	....	9.25	...	140	W.Q. 2000

Ann. = Annealed; Nor. = Normalized; W.Q. = Water Quenched.

These steels may be classified into four groups. The two carbon steels and the 18-8 alloy represent the extremes and are intended to serve as yardsticks in evaluating the properties of the remaining analyses. The third group contains four alloys of the 4-6 Cr-Mo type, differing only in the amounts of special elements present. Lastly, the Cr-Si-Mo steel differs from the 4-6 Cr-Mo analysis in that it contains lower chromium and greater silicon.

All the electric steels were made in commercial arc furnaces. The open-hearth carbon steel is included for comparative purposes. It is believed that in all high temperature work comparisons of different analyses should be made only on steels manufactured by the same process. The properties of the electric furnace carbon steel, rather than the open-hearth steel, have therefore been used in the comparisons.

Rupture Test Results

The results are arranged so as to show the influence of the time required for fracture on the strength and ductility characteristics of the steels, and to compare the rupture strength with the creep and oxidation data obtained at the same temperatures.

Stress Versus Time for Fracture

Tests of this type were conducted at temperatures ranging from 1000 to 1500 degrees Fahr. Fig. 3, setting forth the results from

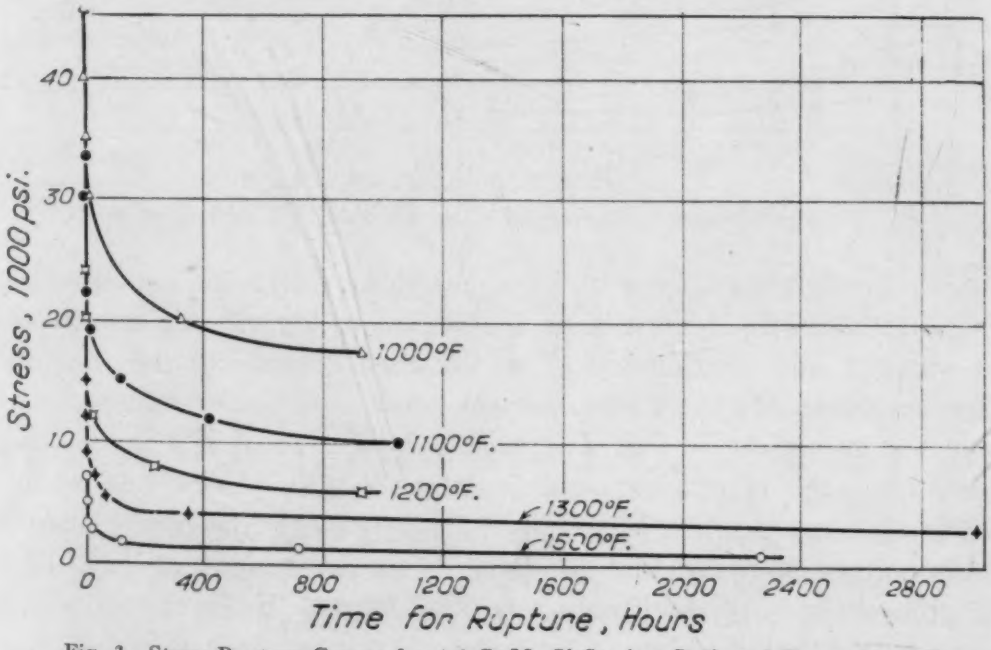


Fig. 3—Stress-Rupture Curves for 4-6 Cr-Mo-Si Steel at Indicated Temperatures.

the 4-6 Cr-Mo-Si steel at five different temperatures, is included as typical of the relationship obtained in all cases between stress and time for fracture when plotted to cartesian coordinates. At each temperature, the shape of the curves gives an indication of the stresses required for prolonged fracture times. For example, on the

basis of the 1300 degrees Fahr. curve it is evident that any stress below 3000 pounds would require an extended time period for actual fracture.

Similarly, Fig. 4 shows typical results for a number of different steels at 1300 degrees Fahr. Even though all the steels, with the exception of the 18-8 analysis, are of the low alloy pearlitic type, marked differences exist in their rupture strength even at this high temperature.

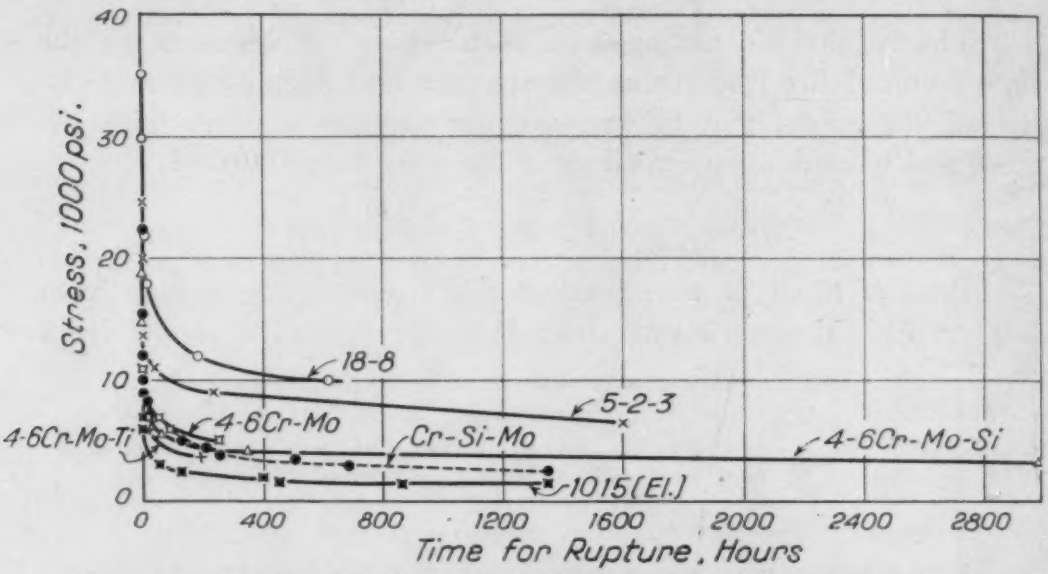


Fig. 4—Stress-Rupture Curves at 1300 Degrees Fahr. for Designated Steels.

Although the curves of Figs. 3 and 4 give an indication of the rupture strength, if the results are plotted to logarithmic coordinates a straight line relationship exists between stress and the time for fracture provided the steel possesses good oxidation resistance under the test conditions. This relationship is illustrated in Fig. 5 which sets forth the results obtained from the 4-6 Cr-Mo-Si steel at five different temperatures. A straight line represents the results at each temperature showing that oxidation was not serious at 1300-1500 degrees Fahr. after approximately 3000 hours. From curves of this type extrapolation to longer time periods can be made safely.

Figs. 6 and 7, showing a few results obtained from the various steels at 1000 and 1500 degrees Fahr., are included as representative of the results obtained at each of the temperatures. As in the case of Fig. 4, marked differences are found to exist between the steels.

A continuous straight-line relationship does not exist between stress and rupture time for all of the steels at these two temperatures.

For example, in the case of the 1015(El) steel at 1000 degrees Fahr. it will be noted that a break occurs in this line at about 2800 hours; after a change in slope, the relationship again becomes a straight line.

The rupture strengths for each of the steels tested are summarized in Table II. The values reported were obtained by logarithmic plotting as discussed previously. While, in certain cases,

Table II

Relationship Between Stress and Time for Rupture for Designated Steels at Indicated Temperatures

Steel	Stress for Designated Fracture Time, Hours 1,000	5,000	10,000	40,000*	100,000*
			1000 Degrees Fahr.		
1015 (El)	12,800	8,800	6,800	4,000	2,800
Cr-Si-Mo	46,500	26,200	20,400	13,100	9,000
4-6 Cr-Mo	19,800	.....	.....	.....	.....
HSi 4-6 Cr-Mo	17,400	14,500	13,200	11,200	10,000
			1100 Degrees Fahr.		
4-6 Cr-Mo	11,400	.....	.....	.....	.....
HSi 4-6 Cr-Mo	10,500	.....	.....	.....	.....
			1200 Degrees Fahr.		
1015 (OH)	2,600	1,700	1,400	980	.....
1015 (El)	2,500	1,500	1,220	800	600
Cr-Si-Mo	7,000	4,700	3,950	2,800	2,200
4-6 Cr-Mo	7,000	.....	.....	.....	.....
HSi 4-6 Cr-Mo	6,200	5,000	4,500	3,700	3,300
			1300 Degrees Fahr.		
1015 (OH)	1,500	980	830	590	.....
1015 (El)	1,400	870	720	480	.....
Cr-Si-Mo	2,700	1,620	1,300	840	.....
4-6 Cr-Mo	.....	.....	.....	.....	.....
HSi 4-6 Cr-Mo	3,700	2,880	2,550	.....	.....
5-2-3	5,600	.....	.....	.....	.....
18-8	9,600	.....	.....	.....	.....
			1400 Degrees Fahr.		
1015 (OH)	900	580	480	335	.....
1015 (El)	700	500	280	165	.....
Cr-Si-Mo	950	370	370	210	.....
			1500 Degrees Fahr.		
HSi 4-6 Cr-Mo	1,180	880	770	.....	.....
5-2-3	2,430	.....	.....	.....	.....
18-8	3,000	1,780	1,400	880	.....

*Tests not necessarily conducted for given time period but actual slope believed to be sufficiently determined to establish stress value.

stresses are reported for fracture times as great as 40,000 hours, no tests were conducted for this time period, the maximum testing time being 14,000 hours. The slope of the logarithmic lines in these cases was, however, believed to be sufficiently well established to permit this degree of extrapolation. The rupture strength, when influenced by oxidation, is dependent on the atmosphere existing in the furnace. These tests were conducted under slightly oxidizing conditions and therefore those applications in which the rate of oxidation would be less or greater would require that a suitable correction factor be used with the rupture strength.

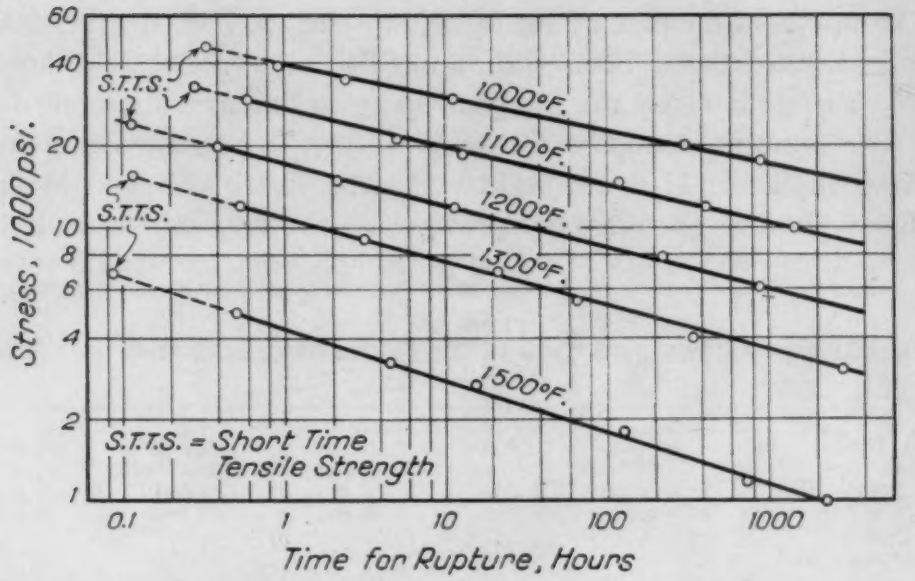


Fig. 5—Stress-Rupture Curves at Indicated Temperatures for 4-6 Cr-Mo-Si Steel.

The necessity of making allowances for oxidation might be considered as a shortcoming of this method but, if so, the same criticism applies to the present-day creep test.

Time for Fracture Versus Ductility

The preceding discussion has considered the stresses required for rupture but has made no mention of the ductility of the fractured specimens. This latter point is of importance as it is the only direct means at present available for judging the extent to which a steel will deform before actual fracture occurs. When it is recalled that in many applications metals are continued in service until relatively large deformations are visible, the importance of ductility before fracture is realized.

The ductile properties of the fractured specimens expressed as per cent elongation in 2 inches are summarized in Table III. The values reported were obtained from the curves resulting from a plot of ductility versus fracture time.

The data of Table III clearly indicate the marked differences in the ductility characteristics of the fractured specimens. The extremes of these differences are shown by the 1015 (El) and the Cr-Si-Mo steels at 1000 degrees Fahr. As the fracture time was extended from a few minutes to 5000 hours the elongation of the carbon steel decreased from an original value of 42.5 per cent to one of 13.0 per

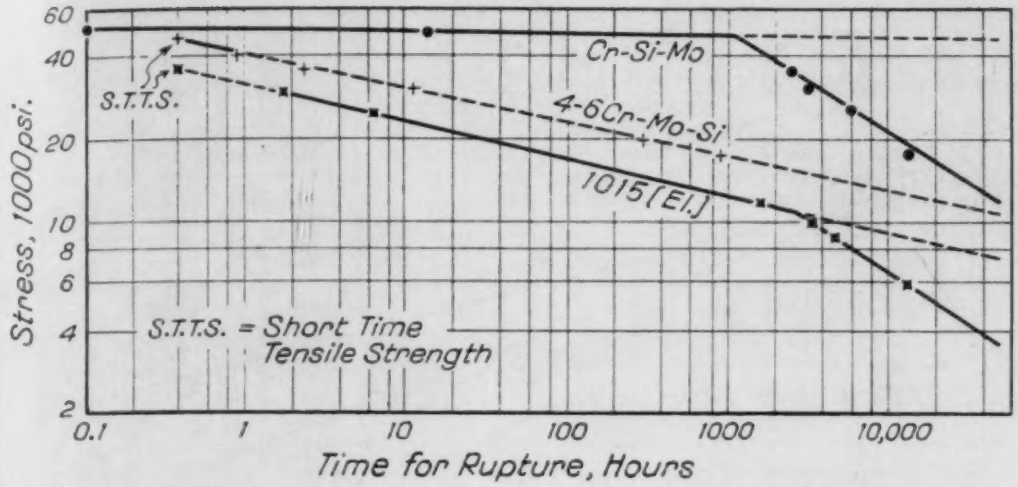


Fig. 6—Stress-Rupture Relationship for Designated Steels at 1000 Degrees Fahr.

cent. On the other hand, the values for the Cr-Si-Mo analysis ranged only from 32.5 to 22.5 per cent. It is significant that with the carbon steel the elongation decreased continuously as the fracture time was extended, while with the Cr-Si-Mo analysis the variations were not uniform.

Likewise, the elongation value of the 18-8 analysis at 1300 degrees Fahr. decreased from 35.0 to 19.6 per cent and at 1500 degrees Fahr. from 33.75 to 12.0 per cent as the fracture time was extended to 300 hours. The 4-6 Cr-Mo-Si steel at these same two temperatures possessed corresponding ranges of only 79 to 74.6 and 106.8 to 88.0 per cent, respectively. On the basis of these findings the 18-8 alloy would rupture without appreciable elongation under prolonged fracture times at 1300 and 1500 degrees Fahr. while the 4-6 Cr-Mo-Si steel, under the same conditions, would show pronounced deformation. These results may be influenced largely by the atmospheres to which the steel is exposed.

Rupture Strength Versus Creep Characteristics

Since the creep characteristics are now commonly used for high temperature design purposes, a comparison of the results from the rupture strength and creep tests should be of interest. The comparison is confined to the very long time rupture tests in order to evaluate properly the effect of time on the steels.

In Table IV are found the long time rupture strength values obtained by extrapolation to 100,000 hours and the creep strengths for a rate of creep of 1 per cent in 100,000 hours for the electric

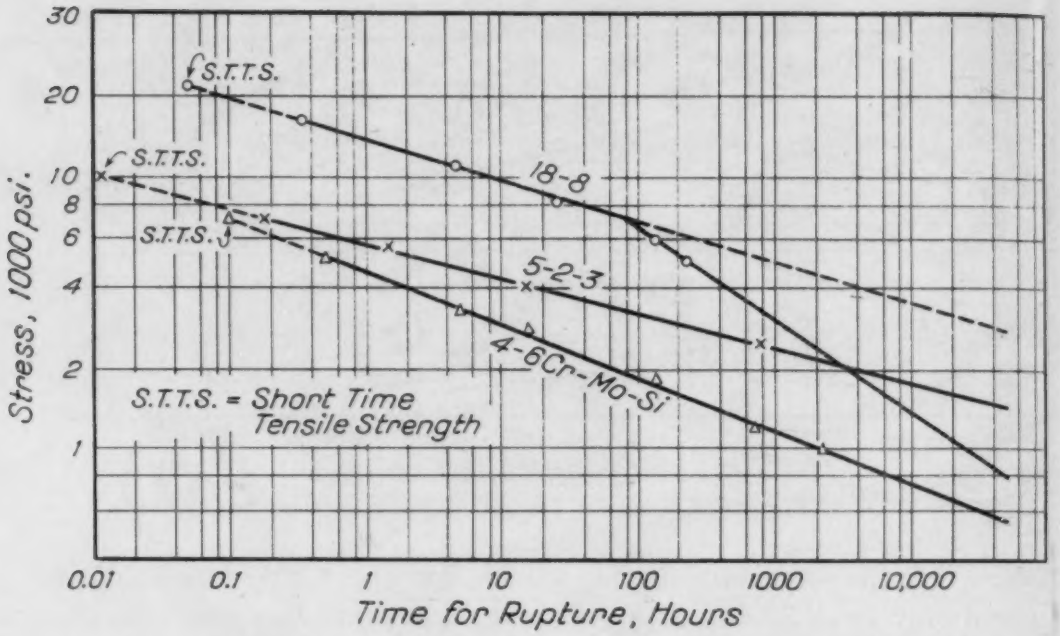


Fig. 7—Stress-Rupture Relationship for Designated Steels at 1500 Degrees Fahr.

furnace carbon steel, Cr-Si-Mo and 4-6 Cr-Mo-Si alloys at 1000 and 1200 degrees Fahr. The rupture strength of the steels seems to be conservative enough to become the basis for designing stresses. In some cases the rupture strength and the creep strength are nearly identical. Perhaps this may be considered as a confirmation of the usefulness of the creep test, even though in certain cases it is indicated that the creep stress for 1 per cent creep in 100,000 hours will cause actual rupture in this time period. This statement is substantiated by the data of Table III, for on the basis of the elongation values it is entirely possible that certain of the steels might undergo only one per cent deformation when 100,000 hours is required for fracture. However, if the two tests could be considered as having equal merit, the rupture test should be preferred because of the simple method of testing involved and the inexpensive equipment required.

Rupture Tests Versus Oxidation Resistance

The appearance of the fractured specimens, and especially those which have required extended time periods for rupture, clearly indicate that the logarithmic relationship between stress and fracture time, as shown in Figs. 5, 6 and 7, must be dependent on the ability of the steel to resist oxidation under the test conditions. For example, in Fig. 5, a continuous straight line relationship was maintained

Table III

Influence of Time for Fracture on the Resulting Ductility of Designated Steels at Indicated Temperatures

		Elongation of Specimens Fractured at Indicated Time Periods, Hours											
1015 (El)	STTS	100	200	300	400	500	1000	1500	2000	2500	3000	5000	10,000
1000	42.5	41.0	39.0	37.5	35.5	34.0	28.0	24.0	22.0	19.5	17.5	13.0	12.0
1200	54.25	30.3	24.0	23.4	22.9	22.0	22.0	22.0	22.0	....	....	....	....
1300	59.5	45.0	40.0	34.9	29.5	26.3	22.0	27.0	....	....	....	....	....
1400	69.75	48.2*	38.0	32.7	30.0	27.0	13.5	....	....	....	....	....	....
1015 (OH)													
1200	70.75	77.5	65.8	64.9	64.0	63.0	58.0	52.1	46.8	41.2	....	....	....
1300	81.25	61.9	57.4	53.0	48.5	45.0	33.1	23.2	13.9	....	....	....	....
1400	79.25	42.0	38.6	38.1	39.0	39.5	42.4	45.5	48.7	....	....	....	....
C1 Si Mo													
1000	32.5	37.3	36.9	36.2	35.9	35.3	33.0	30.5	28.0	25.2	22.5	27.2	....
1200	36.5	61.7	61.0	60.0	56.4	52.8	48.0	41.0	42.0	42.9	44.0	46.0	....
1300	61.75	78.0	71.3	63.0	58.4	53.7	34.1	27.0	....	....	....	....	....
1400	72.25	73.5	65.0	60.0	56.2	53.8	47.6	....	....	....	....	....	....
4-6 Cr-Mo													
1000	28.5	50.5	....	....	....	....	....	....	....	....	....	....	....
1100	38.75	53.8	50.2	46.9	43.4	....	....	....	....	....	....	....	....
1200	46.0	55.0	51.2	46.8	41.5	....	....	....	....	....	....	....	....
1300	65.0	64.5	55.5	46.8	37.5	....	....	....	....	....	....	....	....
4-6 Cr-Mo-Si													
1000	42.75	56.0	56.0	56.0	56.0	56.0	56.0	....	....	....	....	....	....
1100	58.5	64.1	64.0	63.2	62.8	62.8	63.5	....	....	....	....	....	....
1200	70.75	71.8	68.5	68.0	69.0	70.2	76.0	....	....	....	....	....	....
1300	79.0	70.1	72.0	74.0	74.6	73.2	67.1	61.4	56.0	50.0	44.5	....	....
1500	106.8	90.5	89.8	89.0	88.0	87.2	83.2	79.6	76.0	72.2	....	....	....
5-2-3													
1300	53.5	39.1	40.3	41.9	43.0	....	....	....	....	....	....	....	....
1500	82.5	68.5	65.2	62.0	58.8	55.2	39.0	....	....	....	....	....	....
18-8													
1300	35.0	20.2	20.0	19.6	19.0	18.1	....	....	....	....	....	....	....
1500	33.75	20.5	16.2	12.0	....	....	....	....	....	....	....	....	....

at each of the five temperatures, even though certain of the tests at 1300 and 1500 degrees Fahr. were extended to time periods of 2000 to 3000 hours. Furthermore, the fractured specimens showed little, if any, oxidation. On the other hand, in the case of the 1015(El) steel at 1000 degrees Fahr., Fig. 6, a break in the original straight-line relationship occurred at 2800 hours and the specimens exhibited intergranular oxidation.

In order to secure additional information on this subject, oxidation tests were conducted on these steels at 1000, 1250 and 1500 degrees Fahr. The specimens were heated for 1000 hours in closed electric muffle furnaces and the results obtained are shown graphically in Fig. 8.

On comparing the oxidation test results with the rupture test curves, it is apparent that the steels possessing the least resistance to oxidation all showed a break in their logarithmic relationship. Furthermore, the time required to reach this break is longer the better the oxidation resistance. For example, at 1300 degrees Fahr., the

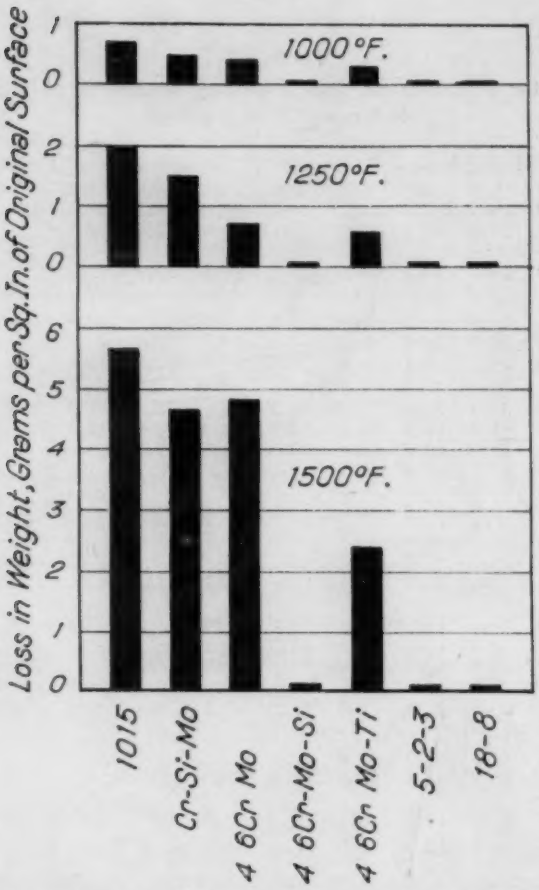


Fig. 8—Comparative Oxidation Resistance of Designated Steels at Indicated Temperatures.

break in the 1015(El) steel occurs at 8 hours, and with the Cr-Si-Mo and 4-6 Cr-Mo analyses at approximately 100 hours.

In addition to general oxidation resistance another type of attack must be considered, namely, intergranular oxidation. From many

Table IV
Relationship Between Long-Time Rupture Strength and Creep Strength

Steel	Temperature Deg. Fahr.	Stress for Rupture in 100,000 Hours	Creep Strength 1 Per Cent in 100,000 Hrs.
1015 (El)	1000	2,800	2,700
Cr-Si-Mo	1000	9,000	13,000
4-6 Cr-Mo-Si	1000	10,000	5,500
1015 (El)	1200	600	290
Cr-Si-Mo	1200	2,200	1,950
4-6 Cr-Mo-Si	1200	3,300	1,600

observations it appears that under certain conditions of time, temperature, stress, and oxidation all steels may be subject to this form

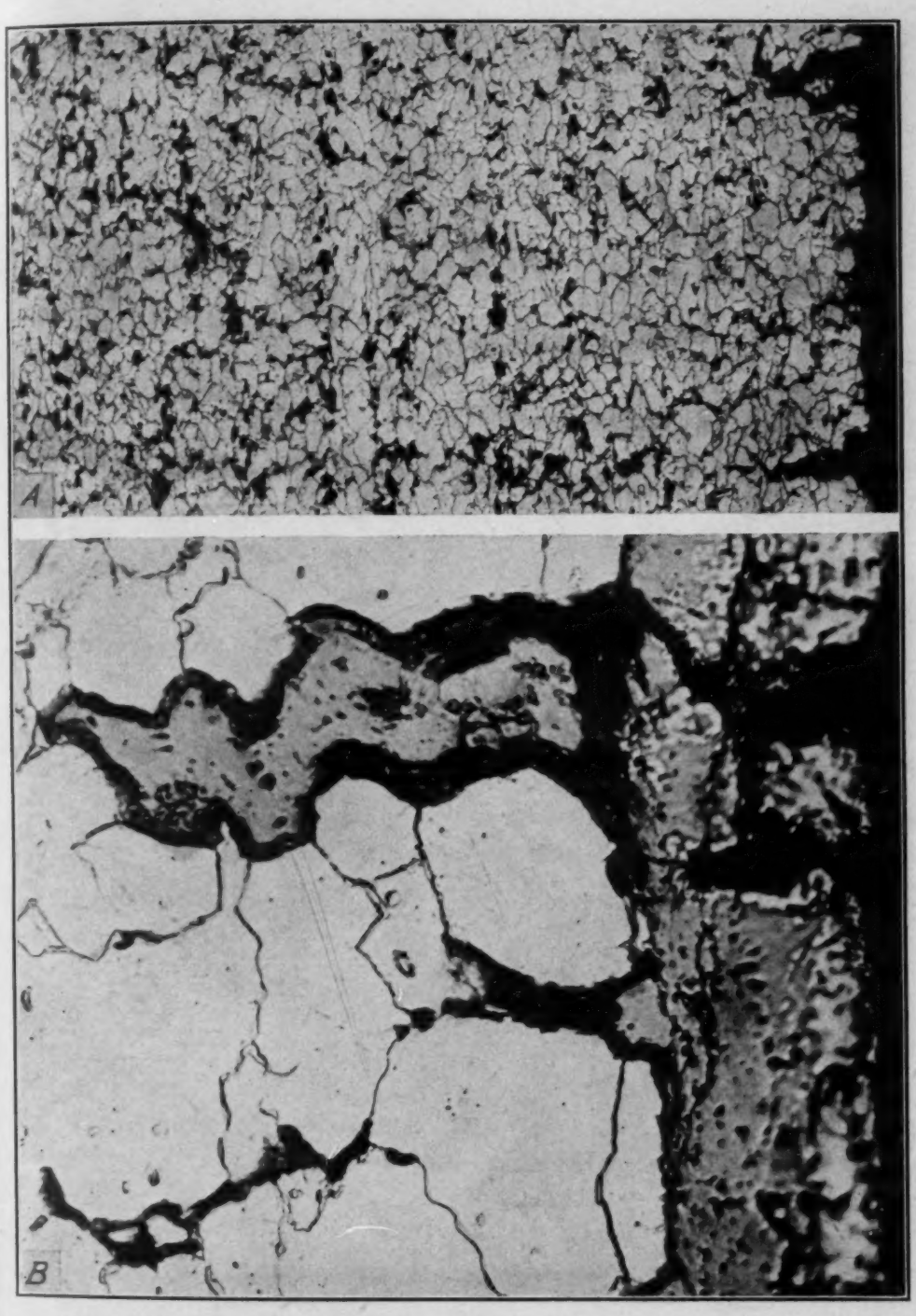


Fig. 9—Microstructures Showing the Intergranular Oxidation of 1015 (El) Steel at 1000 Degrees Fahr. Stress—12,000 Pounds; Time for Fracture—1552 Hours. A—× 100. B—× 1000.

of attack. Under conditions in which the rate of general oxidation is rapid, the intergranular oxidation is obscured by the scaling of the surface. When oxidation is proceeding slowly, however, the inter-

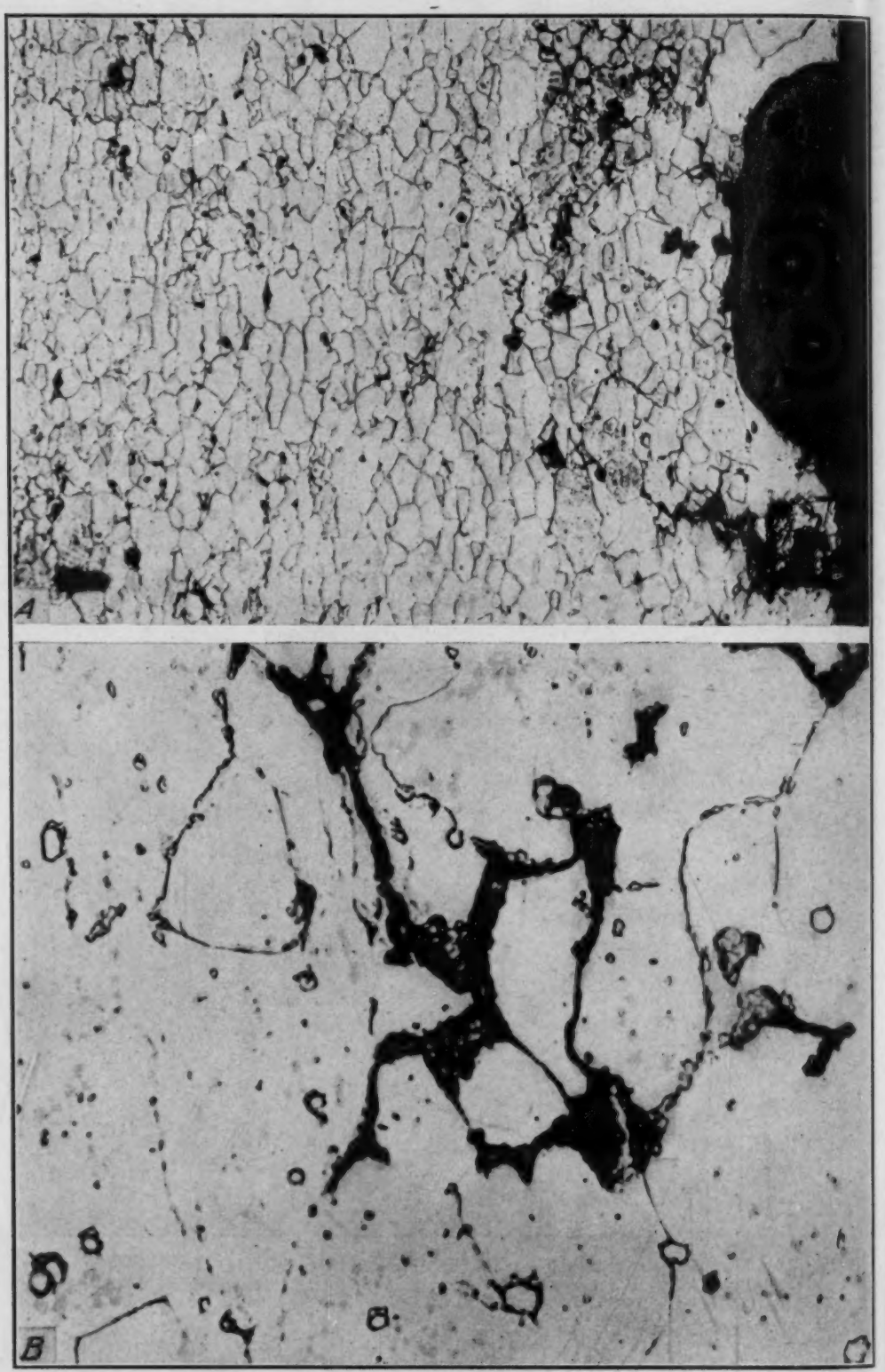


Fig. 10—Microstructures Showing Intergranular Oxidation of 4-6 Cr-Mo-Si Steel at 1500 Degrees Fahr. A—Stress—1000 Pounds; Fracture Time—2268 Hours. × 100. B—Stress—1000 Pounds; Fracture Time—2268 Hours. × 1000.

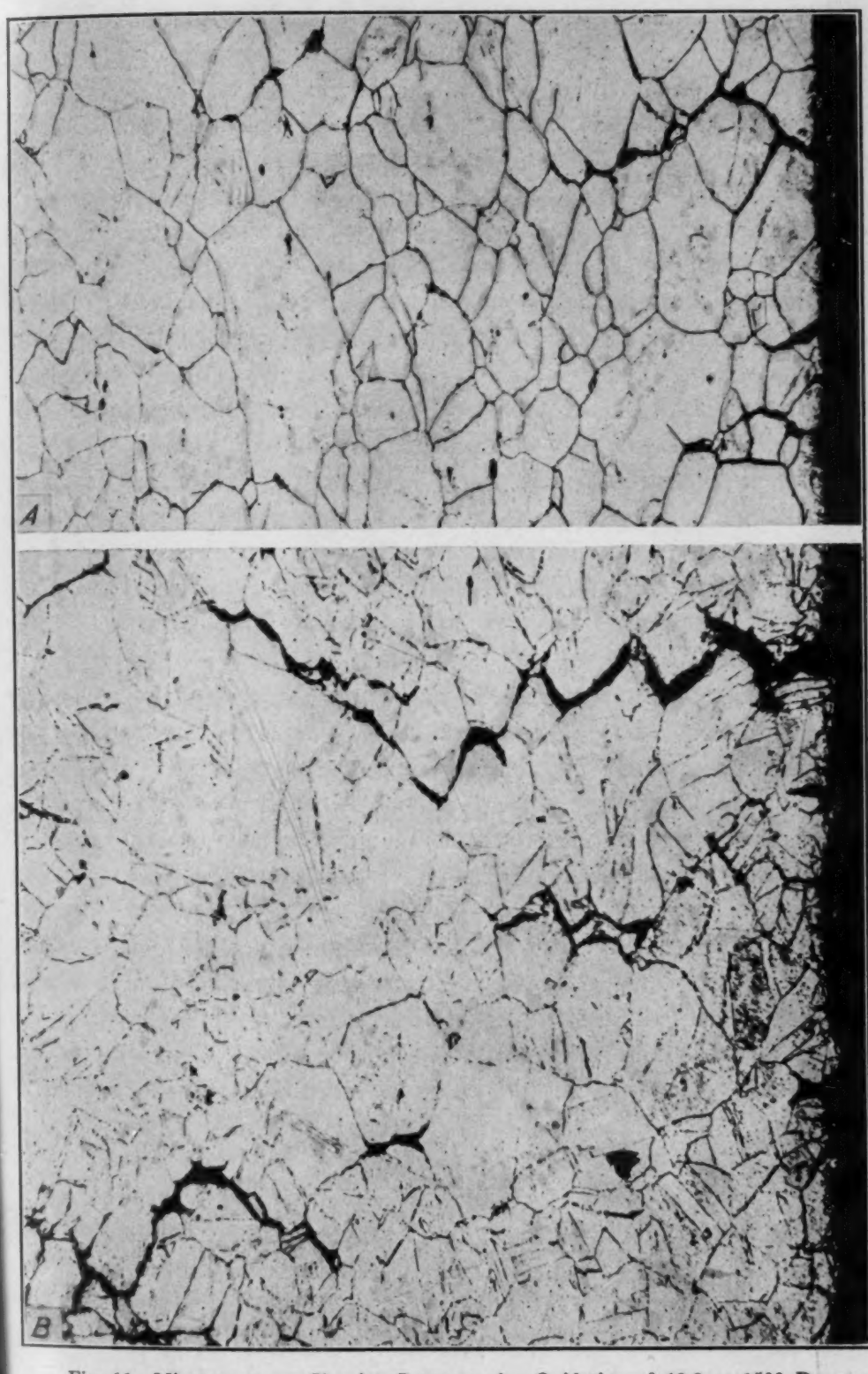


Fig. 11—Microstructures Showing Intergranular Oxidation of 18-8 at 1500 Degrees Fahr. × 100. A—Stress—16,000 Pounds; Fracture Time—0.321 Hours. B—Stress—5000 Pounds; Fracture Time—276 Hours.

granular attack is favored because the grain boundaries offer less resistance than the crystals themselves. The results obtained substantiate this statement.

Plain carbon steels possess fairly good resistance to oxidation at 1000 degrees Fahr., and under the test conditions the surface of the specimens exposed for the longer times in the rupture tests were not badly scaled. Yet, as is evident from the photomicrographs of Fig. 9, pronounced intergranular oxidation occurred in the specimen which required 1550 hours for rupture and this type of attack became even more noticeable after the longer time periods.

The 4-6 Cr-Mo-Si analysis maintained the straight-line relationship under all of the test conditions. The photomicrographs of Fig. 10 show a slight amount of intergranular oxidation in the specimen which required 2268 hours at 1500 degrees Fahr. for fracture, and if longer time periods were used at this temperature the attack might progress to cause a change in the relationship between stress and time for fracture. This steel did not show intergranular oxidation at 1300 degrees Fahr. or for the shorter time periods at 1500 degrees Fahr.

The rate of intergranular attack will be increased by structural changes such as carbide precipitation. This is illustrated by the photomicrographs of Fig. 11, showing the structure of 18-8 after testing at 1500 degrees Fahr. Even when the fracture time was less than one hour, pronounced intergranular attack had already occurred and this was greatly increased as the fracture time was extended to 276 hours.

The occurrence of intergranular oxidation not only changes the logarithmic relationship between stress and fracture time but also greatly decreases the ductility of the fractured specimens, as may be seen in Table III. For this reason a choice of steels not susceptible to this type of attack should be made according to the operating conditions.

Conclusions

The results obtained from the rupture tests on eight steels at temperatures ranging from 1000 to 1500 degrees Fahr. permit the following conclusions:

1. In all cases a direct relationship exists between the stress and time for fracture since when the results are plotted to logarithmic coordinates a straight line is obtained. The ideal relationship con-

sists of a single logarithmic line which may be extended indefinitely. Under actual conditions, however, a change in slope may occur in this relationship due to oxidation.

2. Rupture strength curves based on tests of 2000 to 3000 hours' duration will permit extrapolation to safe long time loading stresses on which high temperature equipment may be designed.

3. The rupture strength in some cases has a value nearly identical with the creep strength for a rate of 1 per cent per 100,000 hours. However, all things being equal, the rupture strength test would be preferred because it is simpler and less expensive.

4. By increasing the resistance to general or intergranular oxidation the long time rupture strength of the steel is increased.

5. Intergranular oxidation not only decreases the long time rupture strength of the steel but also reduces the ductility.

6. Short time rupture tests, not exceeding 200 to 300 hours, may also provide a means for the rapid classification of steels in order of merit, or for acceptance tests on standard materials.

7. The chief merits of the rupture tests are that (a) they serve as a suitable basis for the design of high temperature apparatus in which some deformation of the parts is permissible, and (b) they afford the best means available for determining the ductile properties of steels under the combined action of stress, time and heating.

Acknowledgments

The authors desire to express their appreciation to The Timken Steel and Tube Division of The Timken Roller Bearing Company for the financial assistance which has made these investigations possible and for the permission to publish the findings. Particularly do they wish to express their gratitude to H. H. Timken, Jr. They also wish to acknowledge the valuable assistance of J. W. Freeman in the metallographic investigation.

DISCUSSION

Written Discussion: By Thomas D. Tifft, Sinclair Refining Co., New York City.

The authors of this paper are to be commended on having started the development of a practical method of testing the value of metals for certain classes of high temperature work. As they point out, for services such as still tubes this test is probably much more indicative of the value of the metal than any former test. If, after further development, this test can be shown to give

consistent results it should, in a standard form, be included in the standard specifications. It could replace some of the low temperature physical tests that have no bearing on the value of the metal in its proposed service.

The recorded observations and the conclusions relative to intergranular oxidation occurring after an extended period at high temperature would indicate that present users of metals at these high temperatures can expect an aging effect which will in time cause the metal to lose its ductility and be liable to failure without any elongation and hence without warning. If this is true we, who are users of these alloy metals at fairly high stresses and at fairly high temperatures, should be on the lookout for this aging effect. This is especially important since we frequently are interested in a life of metal many times that of the length of the tests reported.

Our industry, I am sure, would like to know what the authors have to suggest as a practical means of insurance to protect us against the possibility of this intergranular oxidation proceeding until failure might occur without any warning. Is there a means of visual inspection to ascertain this condition or will it be necessary to remove a tube to study it microscopically or physically? Would such a study on one tube indicate the conditions on the balance of the tubes or have our past specifications and inspections permitted variations in structure so great that intergranular oxidation might occur at considerably different rates in tubes presumably the same.

In conclusion I want to thank the authors for having given us some idea on how to develop in the laboratory a safe working stress for metals at high temperature. The volumes of conflicting data on creep have never been of much real help on this most important question.

Written Discussion: By E. S. Dixon, Port Arthur, Texas.

This is a very interesting paper. Whereas creep data published during the last few years have been of little value to the refiner, the results published in this paper are of a practical and usable nature. Creep testing calls for such infinitesimal deformation that refiners have no intention of operating within these limits with respect to preheater tubes. It is a well known fact that heater tubes may swell and may rupture.

Operators are charged with the responsibility of detecting an overheated tube when operating and then reducing the severity of operating conditions. When the unit is shut down the slightly swelled tube is removed from service. This paper gives us a much needed explanation of slow initial creep in heater tubes followed by rapid and apparently accelerated creep. For an example: Tubes are in service for several years; at the end of this period they may be removed because of changes in construction or similar causes. Such tubes are recovered by welding a stub on the end. When these recovered tubes of apparently good quality are replaced in furnace service it is our experience that they rarely have the life of new tubes. Referring to Fig. 1 of the paper, such tubes have been a long time on the road to ultimate failure without detectable bulging. A resumption of service gives relatively early failure although the physicals at room temperature have not been noticeably changed. It may be of interest to know that as a matter of service the 4-6 per cent chromium persists in slow swelling with no sudden rupture; the ductility is always excellent as borne out in Table III under item of Ductility whereas

carbon steel suffers a drop of ductility down as low as 12 to 20 per cent. After 9 years service, it is a well known fact that a 4-6 per cent chromium (no molybdenum) is remarkable in its ability to stand punishment at high temperature. It will swell for long distances along the tube. Tubes may seep oil at a bulge place but they rarely ever rupture so as to cause a fire.

It is believed that this paper explains this very thoroughly. The paper gives a reproduction on a laboratory scale of what we see to be happening to carbon steel and 4-6 chromium (no molybdenum) in full scale operation.

Work of the character presented in this paper should be of real value in appraising the relative merits of various analyses of steels modified somewhat by additions of silicon, molybdenum, etc.

Actual commercial installations of the modified forms of the 4-6 per cent chromium analysis will be followed with interest, particularly with respect to whether or not they will become brittle and rupture after service when being knocked. We are still without an accepted laboratory test to predetermine liability to brittleness when cold after service at high temperature.

Written Discussion: By A. B. Bagsar, chief metallurgist, Sun Oil Co., Marcus Hook, Pa.

The study of the behavior of metals at elevated temperatures is becoming more and more important, since the known facts on this subject have not as yet been definitely correlated into a workable principle or formula, and because more and more engineering applications are developing for metals in high pressure and elevated temperature service.

As clearly stated many years ago by LeChatelier, if a given system is reacted upon by any agency so as to produce a change, a counter reaction ultimately develops within the system tending to minimize or oppose the effect of the change produced. This principle appears to be applicable equally well to animate and inanimate systems. Applying this principle to metals subjected to stress at high temperatures, we see that at certain temperatures strain hardening develops within the metal, tending to oppose the flow or creep of the metal. At some higher temperatures recrystallization occurs in the metal, which tends to oppose strain hardening, and in some cases to retard the rate of creep which would be prevailing if the metal did not recrystallize. In many cases recrystallization may check the susceptibility to premature rupturing. At certain stages zero creep may therefore become possible, and in fact, even a negative creep or contraction may appear theoretically possible in some instances if the reactions opposing creep attain predominance.

It is known that most metals exhibit three stages of creep. These three stages could be profitably analyzed according to the above principle. One deduction would, however, appear to be certain from such analysis, i.e., the creep or flow of metals is not a simple phenomenon. It may be profoundly influenced by internal characteristics of a given metal or a melt of a given metal, which may not be readily discernible.

The authors have presented some valuable data in this paper on the behavior of metals in rupture. According to the data presented, the relationship between time and the rupture strength of a given steel at a given temperature can be represented by a straight line, if logarithmic co-ordinates are used. When high stresses are used and the test coupon ruptures in a short time, con-

siderable energy is undoubtedly spent over and above that required to cause creep or flow. However, the magnitude of this excess energy is obviously less as the time required to cause rupture is increased. It may be that after a considerable amount of creep has occurred, internal discontinuities or fractures develop in the metal due to the presence of inclusions or defects at the grain boundaries, and rupture results without requiring expenditures of much excess energy. It is probably for this reason that the stress required to cause rupture in 100,000 hours is, in some cases, almost identical with the stress computed to cause 1 per cent creep in 100,000 hours.

Several years ago we had the occasion of conducting some tests endeavoring to determine whether or not a relationship exists between the proportional limit of steels and duration of test. A straight line relationship was found, similar to that described for the rupture tests by the authors, with much shorter periods of testing. However, the method used by the authors of this paper is undoubtedly more simple and less expensive.

The authors are to be congratulated for this paper. I believe that the proposed method of rupture tests will find many useful applications enumerated in the paper. Inasmuch as creep characteristics of steels vary considerably from heat to heat of the same approximate chemical analysis, and are also materially affected by variations in heat treatment or casting and finishing temperatures and other factors, the use of the proposed method of rupture tests as an acceptance test may prove to be very advantageous.

Written Discussion: By T. McLean Jasper, A. O. Smith Corp., Milwaukee, Wis.

The above subject has been the consideration of the writer for the past 12 years. The considered temperatures have been, however, somewhat lower than those used by the authors. This has been the result of a contact with the steam and oil cracking industries in which the temperature of the metal is rarely above 1000 degrees Fahr. Although furnace temperatures may be considerably above this value it is very rare that metal temperatures in tubes exceed 1000 degrees Fahr.

The first work of the nature described by the authors is published in the A.S.T.M. Proceedings No. 25, Part II, 1925, and is a discussion by H. J. French of a paper presented by the writer at that period. I might say that this method of arriving at results has been largely responsible for the confirmation of stresses which were used for operating pressure vessels at about 900 degrees Fahr. in the oil industry. It has been the basis for the allowable stress curves now set in the A.P.I.-A.S.M.E. Code for elevated temperatures.

There are several considerations in this method of testing which it is believed should be a part of the testing procedure. Scaling effect in testing should either be eliminated or should be commensurate with the conditions found in the service of the various structures to be considered.

Figs. 9, 10 and 11 of the authors' paper suggest specimens unprotected or very poorly protected against oxidation at high temperatures. A furnace with considerably more or considerably less freedom to the circulation of air might show quite different results from these indicated in Figs. 6 and 7. It is also thought that if the sizes of the specimens were materially changed an entirely different set of curves would result.

The explanation to the break in the loading curve in Figs. 6 and 7 given by the authors seems very logical. It might be suggested that when the question of close clearances in design are important to the engineer, and especially at elevated temperatures, that the moduli of elasticity and of section appropriately applied to bending and torsion is of greater significance than that of creep or strength. If the engineer would meet the demands for stiffness in using the appropriate elastic moduli at a given high temperature he would find generally that the fundamental strength values would decrease less rapidly than the section modulus would increase in value.

Written Discussion: By G. Watts, chief engineer, Standard Oil Company of Indiana.

The report appears to support the belief that the rupture strength test method has possibilities that may lead to its displacement of the creep test method as a means of determining working stresses for parts operating at high temperatures, particularly in those cases in which deformation is not the controlling consideration. The occurrence of breaks in the logarithmic stress-time curves is somewhat disturbing and argues against placing too much reliance on extrapolation to very long service periods from a series of tests which cover a period of not more than 1000 or 2000 hours. Additional tests should be made to ascertain whether the specimens which did not exhibit any break in the stress-time for fracture relationship in the tests covered by the report would have exhibited such breaks if tested for longer periods. It also would be desirable to know whether the specimens which did exhibit breaks in the stress-time for fracture relationship would have shown second breaks had the tests covered longer periods. It should be noted that this shortcoming of the rupture strength test method is also a characteristic of the creep test methods.

It is presumed that the test specimens used in the investigation were standard 0.505-inch diameter specimens. It appears that the breaks in the logarithmic stress-time curves would occur at longer intervals and the slopes of the resulting curves might be quite different if larger specimens were used. It might be worth while to investigate this. Perhaps some part of the variation introduced by the use of various sizes of specimens could be eliminated by calculating the test results on the net unoxidized section of the specimen. If the authors did not do this, it is suggested that it be done to determine whether the breaks in the logarithmic curves would disappear when the maximum penetrations of intergranular and general oxidation were taken into account. In commercial applications some parts may have only one surface exposed, others have all surfaces exposed, and still others have no surfaces exposed. Therefore, from the designer's viewpoint, it is desirable that data on the strength properties of the net section and on the rate of penetration of surface deterioration be kept separate.

There are no recommendations in the report concerning the factor of safety to be used with the rupture strength of a material. It appears that some factor of safety should be used but it may be less than the factor used in low temperature design since in the case of designs based on rupture tests the factor of safety would be applied to a stress producing rupture only after very long exposure to stress, whereas in the case of low temperature design

the factor of safety is applied to a stress which produces rupture in a very short time. It appears further that the factor would vary with the degree of extrapolation. A design for a very long life based on rupture strength data obtained from very much shorter periods of time would require a larger factor of safety than one in which the design life was no greater than the duration of some of the rupture tests. In establishing the factor, consideration should be given to the relationship of the rupture strengths to creep strengths that have been used and are known to be safe.

It will be recalled that the creep strength of parts subjected to poly dimensional stresses is different from (in tubes it is greater than) the creep strength obtained from the usual creep test. It would appear that a similar situation would obtain in the case of rupture strength. The correlation between the simple and poly dimensional cases will materially increase the value of the rupture strength method.

The statement made at the bottom of page 65 can hardly be said to be substantiated by the data of Table III, although it might reasonably be inferred that a deformation of 1 per cent, if taking place in 100,000 hours, could produce fractures. Conclusion No. 2 is open to question; first, because extrapolation to any unexplored field is of necessity speculative, and second, because the authors show that breaks do occur in the stress-time for rupture curves, and there appears to be no method, short of an actual test, by which one can predict where the break will occur. Conclusion No. 6 would appear to be strictly true only in cases where previous tests on other materials of like analysis had shown no break in the stress-time curve for periods of time equal to or in excess of the desired life.

Written Discussion: By Richard F. Miller, United States Steel Corporation, Research Laboratory, Kearny, N. J.

The authors of this article indicate that creep strength values for rates of one per cent per 10,000 hours may be unreliable, and that rupture tests offer a suitable basis for design of high temperature apparatus and are the best means available for determining the ductile properties of steels under the combined action of stress, time, and heating.

It seems to us that these conclusions are somewhat misleading, and that they present an unnecessarily discouraging picture of the creep behavior of steels at elevated temperatures.

Creep rates of one per cent per 10,000 hours may be unreliable if they are determined from short-time creep tests. Such tests are apt to yield an unduly high creep strength for a given steel, and a specimen subjected to such a stress for a longer period of time may soon show an increasing creep rate and fracture. It would be of interest to know the duration of the creep tests which were used in determining the creep strength of 22,000 pounds per square inch for the low alloy steel referred to on page 53.

Rupture tests as described in this paper do not seem to us to disclose the "ideal stress-fracture relationship," since they indicate decreasing ductility with increasing time to fracture. Yet short-time tensile tests made on steel after prolonged service (more than 45,000 hours in an oil still) or after extended creep tests, show that the ductility is then higher than that observed in the original material. Furthermore, long-time creep tests of steel under relatively

low loads show the materials to be quite ductile, and to extend with no indication of intergranular cracking.

On page 55, the authors state that the stress-fracture relationship can be determined from five fracture times covering a total range of 200 to 300 hours. Actually, such short-time tests would not disclose the stress-fracture relationship encountered in service, because insufficient time is allowed for the structural changes which accompany the normal use of a metal at elevated temperatures, and because the stresses are so high and the time is so short that intergranular oxidation and cracking are promoted, and normal flow of the metal by recrystallization and reorientation of the grains is not permitted.

The following inquiries relate to the tests discussed in the present paper.

Steels fractured in high temperature short-time tensile tests show elongated grains and transcrystalline fracture. As the time for fracture is increased. at what point does intercrystalline fracture appear? Does either type of fracture accompanying a given time for fracture or a definite temperature range? Did the carbon steel specimen mentioned on page 53 fracture intergranularly at 13,950 hours, and how much elongation did it show?

Another point needing elucidation is the statement made at the bottom of page 63. It is stated that the time required to reach the break in the logarithmic relationship (between stress and time for rupture) is longer the better the oxidation resistance. In Fig. 6, the break in the curve for 1015 electric furnace steel is at 2800 hours, and the break in the curve for Cr-Si-Mo is at 1000 hours. Yet the chart in Fig. 8 shows oxidation resistance of Cr-Si-Mo to be superior to that of 1015 steel.

Oral Discussion

H. F. Moore:[1] In connection with the study of creep and fracture of very different metals, namely lead and lead alloys, by changing constants it would be possible to use almost the exact words of this paper in giving a discussion of test results. There is one exception. The tests to fracture of lead and lead alloys carried on at the University of Illinois have not gone much beyond 1000 hours, and there have as yet been no evidences of intergranular oxidation with resulting reduction of ductility and strength as shown in the authors' tests on steel. For the lead and lead alloys so far tested there seems to be little reduction of elongation at fracture with increase in length of time required for fracture. An antimony-lead alloy seems an exception to this statement, showing a slight reduction of elongation.

As was brought out in the paper, the question of amount of stretch under long-continued load which can be developed before fracture is of great importance to the designer. I would like to approach this question in a little different way from that set forth in the paper,—not in a contradictory way, just a different way. It has been recognized for some time that in creep to fracture there are three fairly well-marked stages: (1) a relatively rapid adjustment of the metal under steady load, (2) a long period of creep at nearly a constant rate, and (3) a stage of increasing rate of creep which ends in fracture of the specimen. I suggest the study of elongation, not the whole test,

[1]Research Professor of Engineering Materials, University of Illinois, Urbana, Ill.

but the elongation up to the beginning of the third stage, a study analogous to the study of elongation of an ordinary tension specimen up to the beginning of "necking down." This would be, in effect, assuming that when this third stage is entered, the useful "life" of a bolt or a rod or a tube may be regarded as ended.

May I congratulate the authors, and the Society, on this important addition to the literature on creep of metals.

H. LeRoy Whitney:[2] It is predicted that carbon steel will rupture in 100,000 hours at a stress of 2800 pounds, whereas there are numerous structures in operation at much higher stresses that have been operating for a considerable length of time. In other words, we now have carbon steel furnace tubes that have been in operation for seven to eight years with a gas outlet temperature in the neighborhood of 875 degrees Fahr., which would mean a tube wall temperature of 1000 degrees Fahr. or better, and they have invariably corroded to a thinness which would permit them to swell perceptibly before rupture. There are very few cases of rupture of carbon steel tubes without warning.

In the A.P.I.-A.S.M.E. Code, the allowable stress at 1000 degrees Fahr. on carbon steel furnace tubes manufactured in accordance with Manufacturers Standard 100 is 3400 pounds per square inch.

Some of these data in the first paper are at least disturbing. I have the unfortunate job of being chairman of the Subcommittee on Ferrous Materials of the Boiler Code Committee, and it is our job to set the allowable stresses for various material, carbon-molybdenum and other alloys, at elevated temperatures, and just when we think we are getting somewhere, some new data come out, which is quite disturbing. Do not think we do not want the truth—we do. But what I am trying to get at is how we should interpret these data and how they should be used in connection with what we know from practice in applying creep data in design.

In discussing this paper with Mr. Rossheim of our company, we felt that it might have been better to publish this paper leaving out extrapolated figures, and that the authors should caution designers against using the figures given as a basis for design, on account of the comparatively short length of time the materials have been on test, and the danger of using extrapolation as a basis for results over a long period of time. My criticism is not meant to discourage the investigation of the possibility of using rupture strength as an index in design, or as a basis for comparing materials of different analyses. However, unintelligent use of these preliminary extrapolated data may well lead to much unnecessary confusion.

As you know, Dr. White and Dr. Clark particularly, the Prime Movers Committee of the Edison Association have adopted an allowable stress of 8000 pounds per square inch for carbon-molybdenum steel tubes at 950 degrees Fahr. I would like to ask Dr. Clark whether he feels that at 950 degrees Fahr. there is any danger of using this stress and at what rate he figures spheroidization will take place.

A. E. White: It so happens that you are getting a cross section now of

[2]M. W. Kellogg Co., Jersey City, N. J.

this ferrous subcommittee of the A.S.M.E. Boiler Code because Whitney is chairman of it and I happen to be a member of it. Also, we are getting a cross section of the Prime Movers Committee because Whitney has brought that into the discussion and I happen to be a member of that committee.

I think we can safely state that there are a great many variables with regard to the use of steels at elevated temperatures, and therefore until we know all of those variables it is rather difficult to predict what the results will be. For instance, I know that the stress for plain carbon steel at the temperatures in question has been set at either 2800 or 3400 pounds. Yet we must not lose sight of the facts which have been gathered in the data presented in this particular paper. There is no question but what that stress would be conservative and proper if we had no surface conditions taking place. For instance, if we would look at Fig. 6, we would find that the stress for this S.A.E. 1015 carbon steel at 100,000 hours could be extrapolated so it would be well above the 3400 pounds which had been set. That we are getting the 2800 pounds is due to the fact that under the conditions under which we tested we did get oxidation of the surface with resultant material in the lowering of the stress values. We believe that is more or less representative of what takes place in surface conditions, although we recognize there may be a number of operations in which the same degree and amount of surface oxidation does not take place.

With regard to the carbon-molybdenum steel, we do know that it is superior from the standpoint of stress values for a corresponding temperature, especially one above the equicohesive temperatures, to a plain carbon steel. Therefore, we think we are justified in feeling that higher values should be obtained. However, we must not lose sight of the fact that if conditions exist in which oxidation takes place it is possible that in that case we have set values which are too high for stress purposes.

Dr. Whitney calls attention to the point that we did not mention the fact with regard to the rate of spheroidization at 950 degrees Fahr. There has just been completed at the University of Michigan, although no data have been reported with regard to it, quite an extensive investigation dealing with the rate of spheroidization. We know that spheroidization is very rapid, almost instantaneous on plain carbon steels, at around 1300 degrees Fahr. We know that as the temperature is lowered the rate of spheroidization is very materially decreased. So if a plain carbon steel is used at 950 degrees Fahr. and is not initially in its spheroidal state, the time element for spheroidization has so materially increased as to be of very little moment at that temperature. We know that the rate of spheroidization is also decreased—or rather the temperature—with the addition of carbon. That is, a low carbon steel will spheroidize much more readily than a high carbon steel.

We also know that those elements which are carbide forming reduce the rate of spheroidization, so I would say we have nothing to fear from the standpoint of spheroidization, provided the steel is initially put into service in an unspheroidized state, especially a carbon-molybdenum steel at 950 degrees.

H. L. WHITNEY: Evidently you believe that all of these steels operating at elevated temperatures should be normalized and not annealed.

A. E. WHITE: I think we can say yes to that question.

C. L. CLARK: In further reply to the last question of Mr. Whitney's, I think it depends entirely on the type of service being considered as to whether or not a normalizing or annealing treatment should be used. If one is dealing with material in which the maximum operating temperature is not constant, in which the temperature may approach close to the critical, it is believed that an annealing treatment is just as good, if not preferable, to normalizing treatment.

With respect to the apparent discrepancy between the type fracture often obtained in service in a carbon steel and the one showed in the extended-time fracture test, there is no question but what the effect of atmosphere has considerable bearing. Our atmosphere was very slightly oxidizing, which I believe tends to promote intergranular attack, more than though the atmosphere was more severely oxidizing, and that may be one reason why in commercial installations nonductile type fractures are not as common as we would expect them to be, although I understand from certain companies who have had considerable experience that they frequently do have nonductile fractures in carbon steel after prolonged service, around 1000 degrees Fahr.

Written Closure

By C. L. Clark

We are indebted to those who have discussed this paper, especially since the comments and suggestions offered will greatly assist us in continuing this phase of the work. It is very gratifying to note that many are in agreement with our belief that this test possesses possibilities for the evaluation of materials for high temperature service.

The questions raised by Mr. Tifft are most interesting but we regret to state that, insofar as we know, visual examination will not indicate whether or not intergranular oxidation or corrosion is occurring. For the tubes already in service, it will be necessary to remove a tube and subject it to both a metallographic examination and to room temperature physical tests in order to determine the extent of intergranular attack. Furthermore, such an examination of one tube will be representative of all the tubes in the bank only if the service conditions on all of the tubes have been exactly the same and if all the tubes which went into service were exactly the same. Insofar as new tubes are concerned, it is believed that the test procedure herein considered is the most suitable means at the present time for indicating whether or not intergranular attack will occur in service.

Many of the suggestions made by Mr. Watts have been incorporated into our future program. For example, 10,000-hour tests are now in progress on four different steels, two of which showed no break in the logarithmic relationship for time periods up to 2000 hours while the other two did. The results from these tests will indicate whether the trends developed during 2000 hours continue to hold for the more prolonged times. Likewise work is to be done on specimens of varying size and, as a somewhat different angle of approach, on specimens of the same size under at least three different controlled atmospheres. The suggestion of basing the strength characteristics on the unattacked cross-sectional area cannot be used since even in sections appreciably

removed from the actual fracture, intergranular fissuring extended throughout the entire specimen.

The factor of safety to be applied to the stress-rupture results will vary considerably depending, of course, on the fracture time considered, the type service to be encountered, and the desired life. It has been found, however, that for many steels, including the various modifications of the 4-6 Cr + Mo type, the stress required for fracture in 100,000 hours is twice that required for a creep rate of 0.01 per cent per 1000 hours (1.0 per cent per 100,000 hours). It thus appears that a relationship may exist between the results from these two types of test and those who have successfully used creep values for design purposes can likewise use the stress-rupture results with the necessary correction in the safety factor.

Mr. Watts likewise raises the question as to the influence of single versus multiple dimensional stresses. It so happens that a considerable number of tube expansion tests were conducted in our laboratories during 1925 to 1928. It was then found that the stress and corresponding rupture times produced a straight-line relationship when plotted to logarithmic co-ordinates exactly as is now found for the tensile specimens. It is thus apparent that the same type relationship applies although the magnitude of the stress for any given fracture time may vary. In fact the actual values do indicate the tubes to require the higher stresses.

We were pleased to learn from Mr. Dixon that our present results are in general agreement with those obtained in service from the same type steels, and from Professor Moore that the same relationships exist in lead as in steel. Professor Moore's suggestion of basing the comparison on the deformation up to the third stage, rather than the total elongation up to fracture would be interesting but it would defeat one of the main advantages of the present test, namely, its ability to detect decreasing ductility under the combined action of time, temperature and stress.

We can hardly agree with Mr. Jasper's statement that the temperatures considered are above those encountered commercially. This might be true in certain pressure vessel applications but it certainly is not in the case of tubes for cracking stills and especially during the later periods of the operating cycle. We fully agree that the given atmosphere has a considerable bearing on the results and for this reason tests are to be undertaken on three different controlled atmospheres. In the present tests the atmosphere was slightly oxidizing. Modulus values would be ideal for design purposes provided such a property existed. At the more elevated temperatures, however, these values are apparent rather than real. If this were not the case, it would not be necessary to conduct creep tests.

Dr. Bagsar's analysis of the behavior under prolonged testing times is very interesting and valuable. We cannot fully agree, however, that the intergranular failure is due to the presence of defects or discontinuities in the grain boundaries. It is believed that the procedure of deformation at the more elevated temperatures is such that intergranular failure is always to be expected, provided sufficient time is allowed.

In reply to Dr. Miller we had no intention of discrediting the present creep test and in fact are still conducting a large number of these tests in our own

laboratories. We do feel, however, that for many applications the creep test possesses certain limitations and that it must be at least supplemented by other tests before the complete high temperature behavior of a given analysis will be known. The value of 22,000 pounds per square inch reported in the paper was obtained from four creep tests, each of 1000 hours duration.

We cannot agree with Dr. Miller's statement to the effect that the results presented do not represent the "ideal stress-fracture relationship" since in many cases they indicate decreasing ductility with increasing fracture time. In general during high temperature service both the internal structure of the metal and its surface will undergo change, the degree and extent of which depends on the operating conditions and the composition. The main structural change encountered is spheroidization which in general will decrease the resulting room temperature strength properties with a corresponding increase in the ductility. Surface attack, on the other hand, will decrease the ductility, especially if it is intergranular. It is entirely possible that when specimens are taken from tubes which have been in service the attached surface areas are entirely removed during the machining and the resulting room temperature test indicates only the internal structural changes. Likewise specimens which do show appreciable surface attack might not necessarily possess low ductility at room temperature because of the rate of testing. In other words, under rapid testing at room temperature the major deformation and the resulting fracture is within the grains rather than around them.

A misunderstanding apparently exists with respect to the statement that stress-rupture tests up to 200 or 300 hours might be of value in indicating high temperature service. This statement was intended to apply only in those cases in which the complete curve was available for a similar type steel, or in which it was desired to rapidly classify a series of steels of the same general type, or in which it was desired to learn if two steels of supposedly identical composition possessed the same high temperature characteristics.

The time required for the change to occur from a transcrystalline to an intercrystalline type depends entirely on the temperature and composition. In general, the higher the temperature above a given temperature range, which varies depending on the composition, the shorter the time required. The carbon steel specimen referred to did fracture intergranularly and its elongation in 2 inches was 10.0 per cent as compared to 42.5 per cent from the short-time tensile specimen at the same temperature.

In general the statement is correct that the time required for the break to occur in the logarithmic relationship is proportional to the oxidation resistance and this is especially so at the more elevated temperatures. At the lower temperatures other factors, such as the rate of strain-hardening, may occur and this is believed to be the case with the Cr-Si-Mo steel at 1000 degrees Fahr.

Again we wish to thank those who have entered into this discussion and to assure them that their suggestions will, insofar as possible, be incorporated into our further work.

INFLUENCE OF HEAT TREATMENT ON CREEP OF CARBON-MOLYBDENUM AND CHROMIUM-MOLYBDENUM-SILICON STEEL

By R. F. Miller, R. F. Campbell, R. H. Aborn, and E. C. Wright

Abstract

This paper discusses the creep behavior of a variety of structures produced in two steels by different heat treatments prior to creep testing.

The creep testing apparatus and technique is briefly described. Application of least square analysis to the creep data eliminates variation in personal interpretation of the data, and permits the expression of creep rates which are not constant with time.

Specimens of a carbon-molybdenum steel were tested in creep for 3000 hours at 1100 degrees Fahr. after normalizing and after six different tempering treatments. The most creep resistant structure contains a fine shower precipitate. Specimens showing the greatest change of structure during the creep test also show the greatest tendency to assume an increasing creep rate, and structural stability accompanies a constant creep rate. Mechanical tests indicate that time at temperature under stress lowers the strength and slightly increases the ductility.

Creep tests were also carried out on a normalized and tempered chromium-molybdenum-silicon steel at 850, 950, and 1100 degrees Fahr. Little change of structure occurs during the tests except at 1100 degrees Fahr., where some coarsening of the carbides is noted. At 1100 degrees Fahr. annealed material possesses greater creep resistance than that which has been normalized and tempered.

Introduction

KNOWLEDGE of the creep properties of the several original microstructures produced in a steel by different types of heat treatment prior to creep testing, and of the changes of microstructure taking place in the steel during a creep test, are important because the results of the creep tests are used in the design of parts subjected

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. Of the authors, R. F. Miller, R. F. Campbell and R. H. Aborn are members of the staff of the Research Laboratory, U. S. Steel Corp., Kearny, N. J., and E. C. Wright is chief metallurgist of the National Tube Co., Pittsburgh. Manuscript received July 2, 1937.

to a service life of many years at high temperature, during which similar structural changes may occur. Short-time tests are often misleading, since a structure which is not really stable at a certain temperature may have an initially high creep strength, yet the metal may become weaker and begin to flow at an increasing rate after a period of time in service at this temperature.

In order to determine the relative stability and creep resistance of various original structures, creep measurements were made on specimens of a carbon-molybdenum steel at 1100 degrees Fahr. (595 degrees Cent.) after seven different preliminary heat treatments. These heat treatments yielded different initial structures, some of which changed less than others during the test, the more stable of these structures showing a more nearly linear creep rate over a greater range of stress; also, there were wide differences in the stress required for a given instantaneous creep rate at 3000 hours.

Creep tests were also made on a chromium-molybdenum-silicon steel at 850, 950, and 1100 degrees Fahr. (455, 510, 595 degrees Cent.). At the highest temperature, the rate of creep under a given stress was less when the metal had been annealed than when it had been normalized and tempered.

Apparatus and Procedure

The creep testing equipment employed was a modification of the type used at Battelle Memorial Institute (1), (2)[1]. The specimen, having a gage section 0.505 inch diameter x 2.3 inches, was held in cast nonmagnetic adaptors in an electric furnace which had a uniformity of temperature of ± 1 degree Fahr. over the gage length of the specimen during the entire test. The furnace windings were magnetically opposed and thus noninductive; measurements indicated that the resultant magneto-striction in the specimen was negligibly small.

The standard period of test adopted for this investigation was 3000 hours, or 4½ months. The amount of extension of the specimen was measured at least twice a week by each of two observers using a microscope with a calibrated filar eyepiece, the least division on which was 0.00005 inch. The microscope was focused on reference marks engraved on pairs of platinum strips, attached to the specimen 180 degrees apart, permitting measurements to be made both from the front and from the back of the machine.

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

Daily checking of the microscope against a standard length, daily measurement of the temperature of the specimen with a semi-precision potentiometer accompanied by an automatic continuous record of the specimen temperature, periodic checking of the thermocouples, and careful calibration of the machines for lever ratio, friction losses, and actual value of the loading weights, enabled the extension measurements to be made with an error not greater than $\pm$ 0.0065 per cent.

The procedure employed in testing a specimen was as follows: The furnace was checked for temperature uniformity at the test temperature for one week with a dummy specimen carrying five thermocouples, and was used only if the temperature was uniform within $\pm$ 1 degree Fahr. over the gage length. The actual specimen was installed, and specimen and furnace allowed to come to temperature equilibrium at the temperature of the test for one week; the load was then applied, and regular readings of extension were made as previously indicated. At the end of the test period, the load was relieved and the specimen allowed to cool; the scale was removed, and the final diameter measured. The specimen was then subjected to hardness, impact, and tensile tests, and sectioned for micro-study. The same measurements were made on the initial material so that direct comparisons could be made to determine the effect of exposure under the conditions of the test upon these properties of the metal.

Analysis of the Observations

In the observations from day to day of the slow extension of a specimen under load at high temperature, there will inevitably be apparent irregularities which appear as deviations from a smooth curve when extension is plotted against elapsed time. Even when the actual creep rate is of the order of 1.0 millionths inch per inch per hour[2]—and this is the highest rate which could be extrapolated with any degree of assurance—these accidental deviations are of the same magnitude as the real extension from day to day. Consequently there is always difficulty in deciding whether the curve which best represents the data should be a straight line or a parabola, and which curve of a given form is best; and in general two men, working independently, will reach somewhat different conclusions.

[2]Creep rates may also be expressed in per cent per 1000 hours. 1.0 millionths in./in./hr. (1.0×10^{-6} in./in./hr.) is equivalent to 0.10 per cent per 1000 hours.

To obviate this uncertainty in interpretation of the observations, use was made of the well-known method of least squares, which is independent of any personal predilection and yields the constants in the equation of a curve of any specified form which best represents all of the observations.

The principle of the method is that the data are best represented by that curve for which the sum of the squares of the deviations of the observed points from it is a minimum. Its application, which is described in detail in many mathematical books (3), (4), is simple and soon becomes a routine procedure, particularly if a calculating machine is available. In the present tests, the first 500 hours were considered as an initial adjustment period, and observations made during this period were omitted from the calculations. The least square analysis was carried through for the time period 500-3000 hours to determine the best values for the constants (a b c d and e) both for the linear equation $l = a + bt$ (where l is the gage length of the specimen and t is elapsed time in hours) and for the parabolic equation $l = c + dt + et^2$. When the computed value of e is less than corresponds to the experimental error of the observations, and hence can be regarded as zero, the two equations are identical; in other words, a straight line suffices to represent the data. When the probable error of the parabolic curve is less than that of the straight line, both as derived by the method of least squares, the data are best represented by a parabola; and the creep rate is increasing or decreasing with elapsed time according as the computed value of e is positive or negative.

By the procedure just outlined, it is possible to make separate computations, for both the linear and the quadratic equation, for the data of each observer, and for the observations of each observer on the front and the back of each specimen. The results of these comparisons show conclusively that with the present equipment the values of the creep rate, as derived by the method of least squares from the several series of observations, agree within 4 per cent over the test period when the rate is faster than 0.4 millionths in./in./hr.

Practically all published data on creep rate have been derived from a plot of the observations by passing what seemed to the author to be the best straight line through the points for a certain time interval. In order to show that this method may be misleading, particularly when extrapolated to longer time intervals, values of

creep rate, as derived graphically and as computed by the method of least squares, are listed in Tables I and III for all the specimens tested. The difference between these values, as given in column 8, is small when the rate is low and constant, but becomes significant when the rate is increasing (accelerated). Thus the simple graphical method is not well suited to the accurate evaluation of a creep rate which is not in fact constant with time.

Results of Tests on Carbon-Molybdenum Steel

The composition of the open-hearth carbon-molybdenum steel employed in these tests was 0.11 per cent carbon; 0.47 per cent manganese; 0.010 per cent phosphorus; 0.014 per cent sulphur; 0.17 per cent silicon and 0.54 per cent molybdenum. All specimens were from a single billet. The heat treatments selected for the different series before creep testing were:

(A) ½ hour 1650 degrees Fahr., air cool
(B) ½ hour 1650 degrees Fahr., air cool; temper 5 hours 1200 degrees Fahr., air cool
(C) ½ hour 1650 degrees Fahr., air cool; temper 168 hours 1200 degrees Fahr., air cool
(D) ½ hour 1650 degrees Fahr., air cool; temper 5 hours 1300 degrees Fahr., air cool
(E) ½ hour 1650 degrees Fahr., air cool; temper 168 hours 1300 degrees Fahr., air cool
(H) ½ hour 1650 degrees Fahr., air cool; temper 5 hours 1400 degrees Fahr., air cool
(M) ½ hour 1650 degrees Fahr., air cool; temper 168 hours 1400 degrees Fahr., air cool

All the tests on these specimens were carried out at 1100 degrees Fahr. (595 degrees Cent.) for approximately 3000 hours. A list of the individual specimens tested, the duration of the tests, the stresses employed, and the corresponding creep rates and mechanical properties will be found in Table I. The tensile tests were made at room temperature on standard specimens having a gage section 0.505 inch diameter x 2 inches long, and the impact specimens were of the modified Charpy key hole type, 10 x 6-2/3 x 55 mm. Differences in creep behavior and in mechanical properties of this carbon-molybdenum steel subjected to different heat treatments are definitely associated with differences in microstructure. In order to avoid repetition in the following discussion of the individual treatments, the structure of the steel after the preliminary heat treatment and before being held for the test period under stress at high temperature will be called the "initial" structure, in contrast to the structure of the steel after the test period under stress at high temperature, which will be referred to as the "final" structure.

The instantaneous creep rate at 3000 hours, calculated by least square analysis for the specimens of carbon-molybdenum steel is

plotted in Fig. 1 as a logarithm against stress. This type of plot is used merely as a convenient way of separating on the diagram the lower creep rates which on rectangular co-ordinates would be so close together as to be barely distinguishable. The instantaneous rates for specimens similarly heat treated have been connected by straight lines.

Treatment A — The initial normalized structure, shown in Fig. 2a, consists of fine pearlite and ferrite. The Rockwell B hardness is 69, the ultimate strength is 63,000 pounds per square inch, and the impact strength is 50.5 foot-pounds. Fig. 2b shows the final structure of the same steel. The pearlite has been largely spheroidized, and migration and agglomeration of the pearlitic carbides at the grain boundaries is noted. Throughout the ferrite

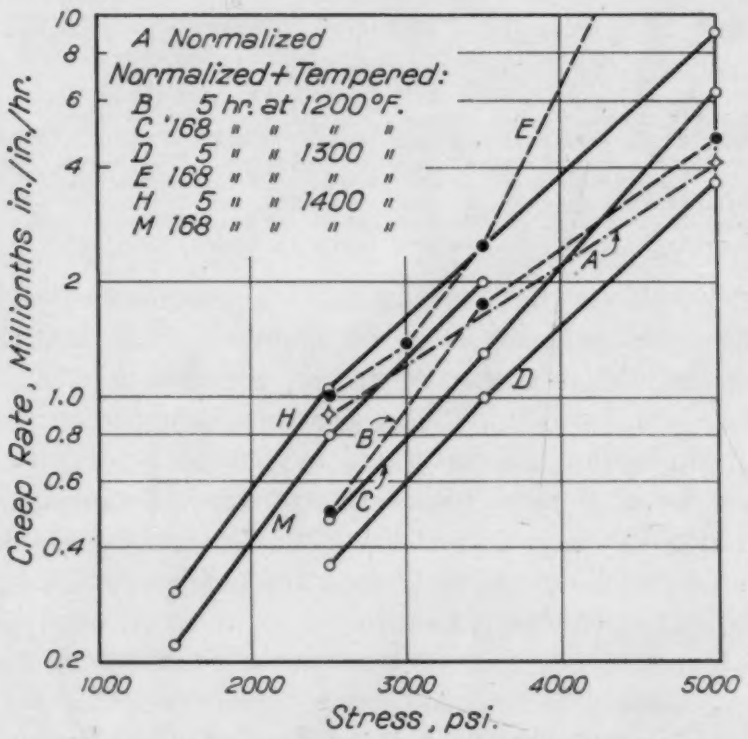


Fig. 1—Influence of Heat Treatment on Creep of 0.11 Per Cent Carbon, 0.54 Per Cent Molybdenum Steel at 1100 Degrees Fahr., Semi-Log Representation.

groundmass there is a shower precipitate which appears to be distinctly different in behavior from the pearlitic carbides. The hardness has been increased by the period at elevated temperature under stress, and the impact strength and tensile strength have been decreased. The results of the individual tests are listed in Table I, and are shown in diagrammatic form in Fig. 6. By interpolation

Table I
Results of Tests on Carbon-Molybdenum Steel

Table 1
Results of Tests on Carbon-Molybdenum Steel

Spec. No.	Temp. of Test °F	Stress on Specimen during Creep Test PSI	Duration of Creep Test hrs.	Total Elong. during Creep Test %	Least Square Creep Rate at 3000 hrs. millionths in./in./hr.	Graphical Creep Rate during last 1000 hours millionths in./in./hr.	Diff. between Graph. and L. S. Creep Rates	Hard. Rock. B	Ultimate Tensile Strength PSI	Per Cent Elong. in 2"	Reduction of Area Per Cent	Impact Strength ft. lbs.
A5	Room	Original Material						69.2	63,000	37.0	74.5	50.5
A1	1100	2500	2360	0.269	0.90	1.08	0.18	...	54,750	43.0	77.9	...
A4	1100	4500	2450	0.556	2.83	2.44	0.39	73.2	.....	...	...	40.5
A2	1100	5000	3530	1.07	4.00	3.58	0.42	...	58,000	32.0	77.0	...
B4	Room	Original Material						71.6	59,000	38.5	76.8	52.0
B1	1100	2500	3210	0.184	0.50	0.60	0.10	70.5	.....	...	...	40.0
B3	1100	3500	3000	0.566	1.80	1.81	0.01	...	56,700	40.0	76.6	...
B5	1100	5000	2670	....	4.63	3.26	1.37	66.5	.....	...	...	39.5
C4	Room	Original Material						74.4	59,000	37.5	77.0	50.0
C1	1100	2500	3080	0.145	0.47	0.53	0.06	65.2	.....	...	...	39.0
C3	1100	3500	5140	0.694	1.29	1.44	0.15	...	54,000	40.0	76.0	...
C2	1100	5000	3000	1.390	6.15	5.63	0.52	68.0	.....	...	...	40.5
D4	Room	Original Material						68.2	58,200	39.0	78.8	51.0
D1	1100	2500	3020	0.134	0.36	0.35	0.01	66.5	.....	...	...	39.5
D3	1100	3500	3120	0.321	0.98	0.96	0.02	...	55,000	40.0	76.4	...
D2	1100	5000	3120	0.444	3.58	3.35	0.23	68.4	.....	...	...	44.0
E4	Room	Original Material						65.8	56,000	36.0	64.7	28.0
E6	1100	2500	3030	0.354	1.03	0.87	0.16	61.6	.....	...	...	25.5
E7	1100	3000	3140	0.484	1.38	1.36	0.02	...	53,500	41.0	70.2	...
E5	1100	3500	3070	0.790	2.46	2.35	0.11	65.7	.....	...	...	24.0
E3	1100	5000 7500	4200	103.0	14.20	12.77	1.43	...	Fractured	...	...	...
H4	Room	Original Material						74.4	62,000	38.0	76.9	54.0
H3	1100	1500	3000	0.221	0.66	0.46	0.20	...	56,800	39.0	75.3	...
H1	1100	2500	3050	0.309	1.05	1.28	0.23	70.4	.....	...	...	36.0
H2	1100	5000	3340	2.070	8.81	7.59	1.22	67.3	.....	...	...	39.0
M4	Room	Original Material						71.6	62,100	38.0	77.6	52.0
M3	1100	1500	3000	0.088	0.22	0.13	0.09	...	55,400	39.5	76.7	...
M1	1100	2500	3000	0.216	0.80	0.59	0.21	77.4	.....	...	...	31.0
M5	1100	3500	3020	0.545	2.00	1.78	0.22	...	54,300	42.5	76.0	...

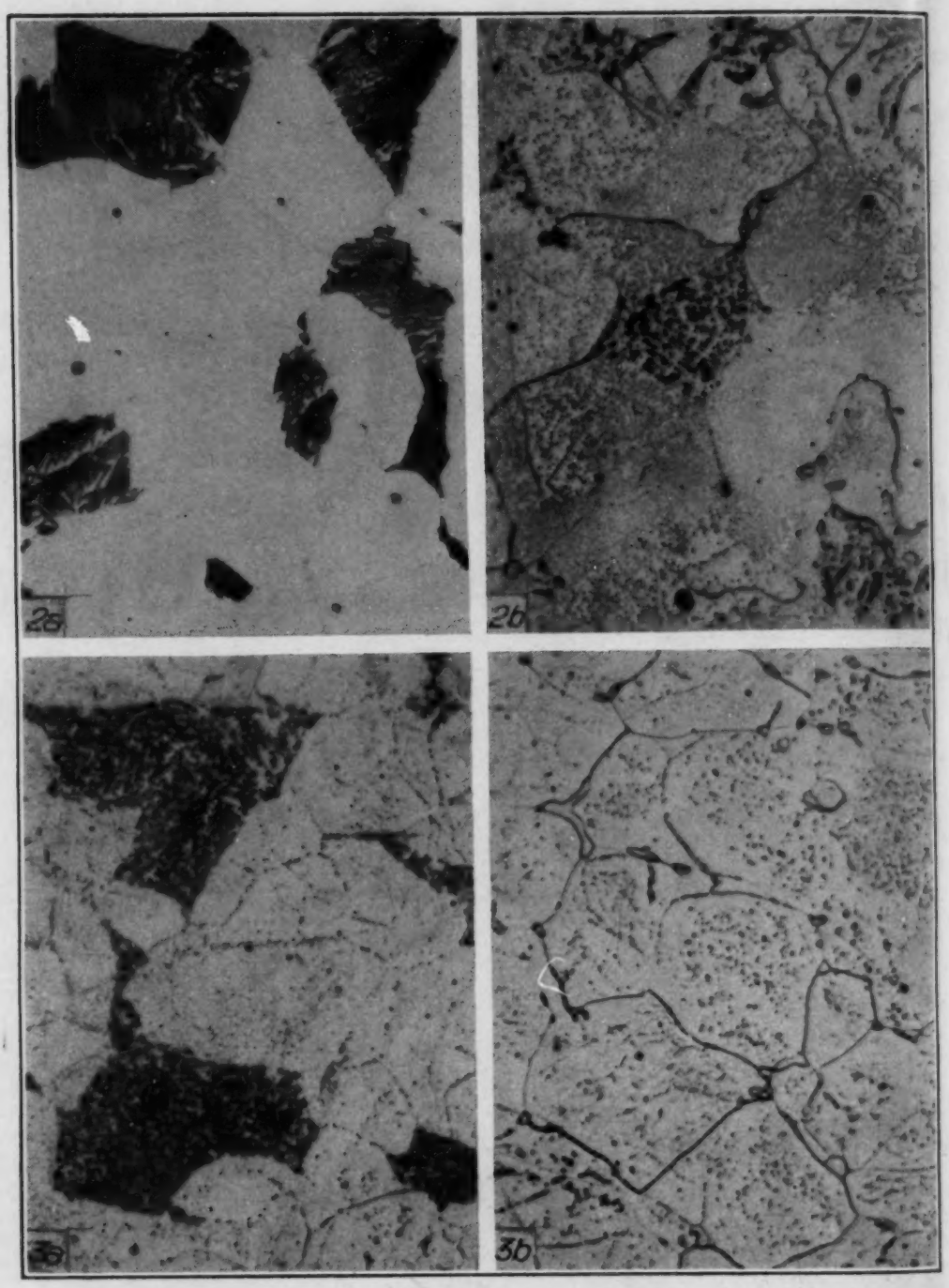


Fig. 2—Carbon-Molybdenum Steel Normalized from 1650 Degrees Fahr. (A treatment) × 1000.
(a) Initial structure before creep test.
(b) Structure after 2450 hours at 1100 degrees Fahr. under a stress of 4500 pounds per square inch.

Fig. 3—Carbon-Molybdenum Steel Normalized and Tempered for 168 Hours at 1200 Degrees Fahr. (C treatment) × 1000.
(a) Initial structure before creep test.
(b) Structure after 3000 hours at 1100 degrees Fahr. under a stress of 5000 pounds per square inch.

from Fig. 1, it is found that a creep rate of 1.0 millionths in./in./hr. is produced in the "A" structure by a stress of 2700 pounds per square inch.

Treatment B — The initial microstructure of the "B" series (normalized, then tempered for five hours at 1200 degrees Fahr.) appears to be quite similar to that of the "A" series, except that the pearlite is slightly spheroidized and there are traces of an intergranular precipitate. The tensile strength of the initial "B" material is somewhat lower than that produced by the normalizing "A" treatment, but the hardness and impact strength are slightly higher. (See Fig. 6.) This increase of hardness corresponds to the increase of hardness of the "A" series after a period of time under stress at high temperature; it appears that the groundmass precipitate which is visible in Fig 2b may have already started to form in the initial "B" structure.

The final "B" structure shows more spheroidization in the original pearlite areas than does the final "A" structure, and the groundmass precipitate is more agglomerated. The hardness, impact strength, and ultimate strength have been decreased by the time at temperature under stress, and this trend is also evident in treatments C, D, E, and H. Examination of Fig. 1 discloses that up to a stress of 3400 pounds per square inch the "B" structure has superior creep properties to the "A," and above that stress the reverse is true. By interpolation, it is found that a stress of 3000 pounds per square inch is required for a creep rate of 1.0 millionths in./in./hr.

Treatment C — The influence on the microstructure of tempering the normalized material for one week at 1200 degrees Fahr. (650 degrees Cent.) is shown in Fig. 3a. The pearlite areas have been almost completely spheroidized, but are still distinguishable. A groundmass precipitate, similar though less pronounced than that seen in the final "A" structure, has been developed in the former clear ferrite areas; part of this precipitate tends to form chains within the grains. The hardness is greater and the tensile and impact strength are somewhat lower than in the initial "A" structure. Fig. 3b shows the final "C" structure. The former pearlite areas have disappeared, the carbides have been spheroidized and are noticeably agglomerated at the grain boundaries in large, angular masses, and the shower precipitate has become coarser. A stress of 3250 pounds per square inch is required for a creep rate of

1.0 millionths in./in./hr. showing superior creep resistance over "A" or "B" at this rate of creep. (See Fig 1.)

Treatment D — Fig. 4a shows the influence on the normalized structure of tempering for five hours at 1300 degrees Fahr. (705 degrees Cent.). The pearlite areas are not as completely spheroidized as in the initial "C" structure, and the shower precipitate in the ferrite matrix is in a fine state of dispersion. The initial hardness and tensile strength are slightly lower than in "A," "B," or "C," and the impact strength is about the same. The final "D" structure is shown in Fig. 4b. The grain boundary carbides are not as large as in the final "C" structure, and the groundmass precipitate has not agglomerated to such a large extent. Examination of Fig. 1 shows that the stress for a creep rate of 1.0 millionths in./in./hr. is 3500 pounds per square inch, the highest for any of the treatments. Furthermore, it will be noted that the "D" treatment produces a material which has superior creep resistance over the whole range of stress examined.

The low creep rate seems to be associated with the particle size and the degree of dispersion of the shower precipitate in the ferrite groundmass. The final "D" structure (Fig. 4b) shows slight coarsening of the shower precipitate, and the durability of the initial beneficial distribution of the dispersed particles beyond 3000 hours while the material is in service or in a creep test under stress at high temperature is not known. A check test is now being run.

Treatment E — Fig. 5a shows the influence on the normalized structure of tempering for one week at 1300 degrees Fahr. (705 degrees Cent.). The spheroidization is seen to be more complete than in any other of the pre-treatments. The pearlite areas have disappeared, the carbides have largely migrated to the grain boundaries, and the groundmass shower precipitate has noticeably coarsened. The structure is in many ways similar to the final "C" structure. The hardness, tensile strength, and impact strength of the initial "E" material are lower than those of the other original structures. The reason for the markedly lower impact strength is possibly due to the grain boundary segregation of the carbides, which gives, in effect, a relatively brittle though soft material. In the final "E" structure, Fig. 5b, the shower precipitate has still further coalesced and the migration of the carbides to the grain boundaries and their agglomeration into large masses is almost complete.

Fig. 4
grees Fahr
(a
(b

Fig. 5
Degrees Fa
(a
(b

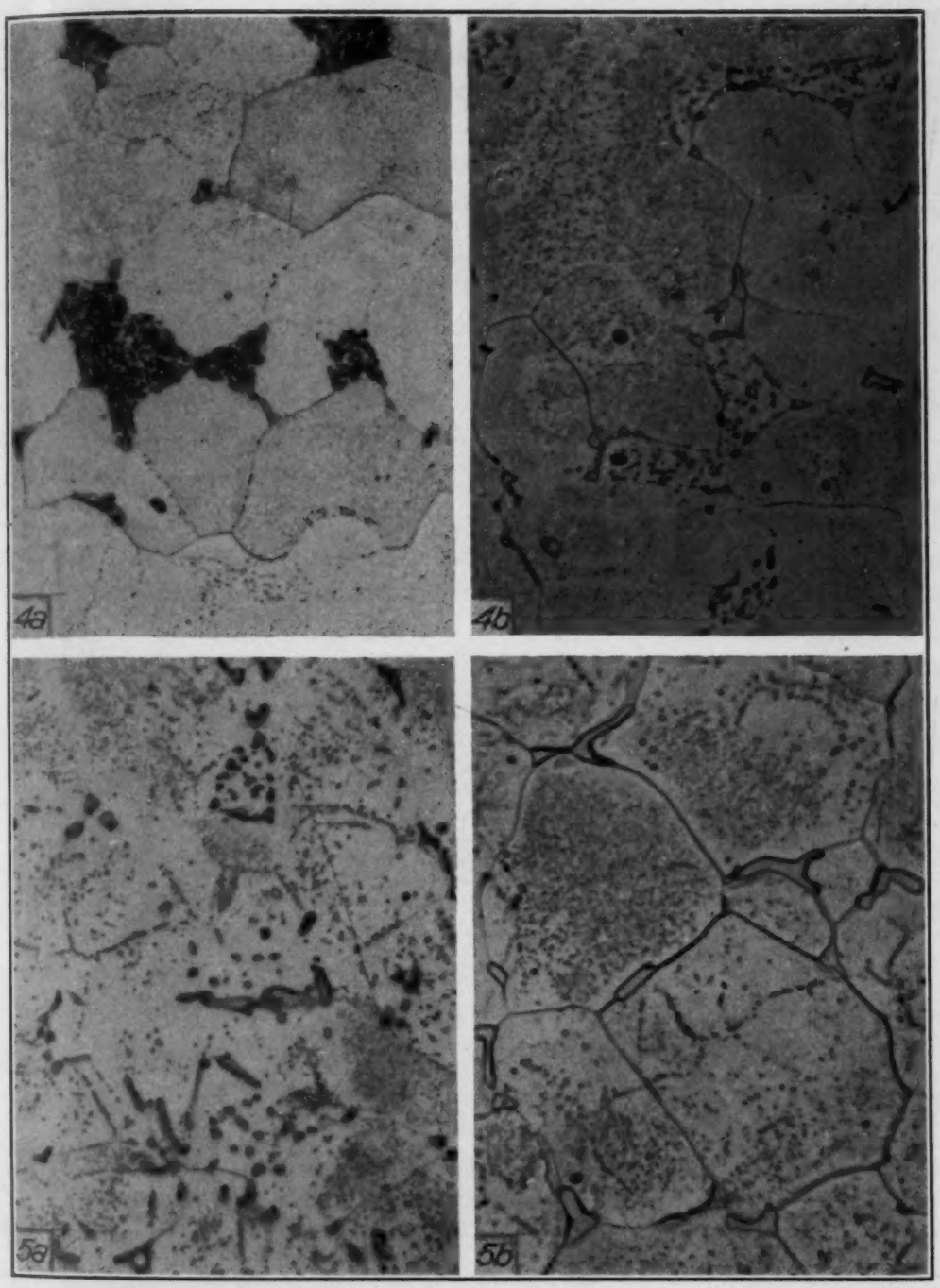


Fig. 4—Carbon-Molybdenum Steel Normalized and Tempered 5 Hours at 1300 Degrees Fahr. (D treatment) × 1000.
(a) Initial structure before creep test.
(b) Structure after 3120 hours at 1100 degrees Fahr. under a stress of 5000 pounds per square inch.

Fig. 5—Carbon-Molybdenum Steel Normalized and Tempered 168 Hours at 1300 Degrees Fahr. (E treatment) × 1000.
(a) Initial structure before creep test.
(b) Structure after 3070 hours at 1100 degrees Fahr. under a stress of 3500 pounds per square inch.

Fig. 1 shows that the creep resistance of the material resulting from the "E" treatment is inferior to that resulting from any other treatment. The stress for a creep rate of 1.0 millionths in./in./hr. is 2500 pounds per square inch, and the creep rate increases rapidly with further increase of stress. Evidently, in the original "E" material, the shower precipitate has coarsened to such a degree that it is no longer as effective in raising the creep strength.

The specimen of the "E" material tested under a stress of 5000 pounds per square inch (E3) exhibited an extremely high creep rate. At the end of 3000 hours, the stress was increased to 7500 pounds per square inch to cause the specimen to creep to failure, which occurred at 4200 hours. A cross section of the specimen showed the fracture to be trans-crystalline, and no evidence was found of intergranular oxidation or cracking.

Treatments H and M — Normalized structures somewhat similar to "A" (Fig. 2a) with no evidence of shower precipitate are produced by both the "H" and "M" treatments, showing that 1400 degrees Fahr. (760 degrees Cent.) is above the A_1 temperature for this steel. The initial tensile strength of these materials is only slightly lower than that of "A", but the impact strength and hardness are slightly greater, perhaps due to the early stages of formation of the shower precipitate in the untransformed ferrite matrix, as was mentioned in the discussion of the "B" treatment. Fig. 1 shows that these structures require stresses of 2450 and 2750 pounds per square inch for a creep rate of 1.0 millionths in./in./hr. and that their creep resistance is slightly inferior to that of "A". Final microstructures of the "H" and "M" series are similar to the final "D" structure, and the pearlite areas are more completely broken up than in the final "A" structure.

Discussion of Results of Tests on Carbon-Molybdenum Steel

Examination of the original and final microstructures makes possible the following comparisons. Tempering the normalized ("A") material for one week at 1200 degrees Fahr. (650 degrees Cent.) (C treatment) produces a structure quite similar to that produced in the normalized ("A") material by 3000 hours at 1100 degrees Fahr. (595 degrees Cent.) under stress. Also, tempering the normalized material for one week at 1300 degrees Fahr. (705 degrees Cent.) (E treatment) produces a structure similar to that

developed in the original "C" material by 3000 hours at 1100 degrees Fahr. (595 degrees Cent.) under stress.

The present creep tests do not permit us to state definitely whether the changes evident in the final as compared with the initial microstructure of the specimens are due mainly to the influence of time at temperature or in part to the influence of stress. According to present indications, the influence of stress is secondary; but in order to determine this point, specimens of this steel variously pretreated are now being held for 3000 hours at 1100 degrees Fahr. under no stress.

The ferrite grain size is 6-7 in the initial structures produced by the seven preliminary heat treatments, as measured by the A.S.T.M.

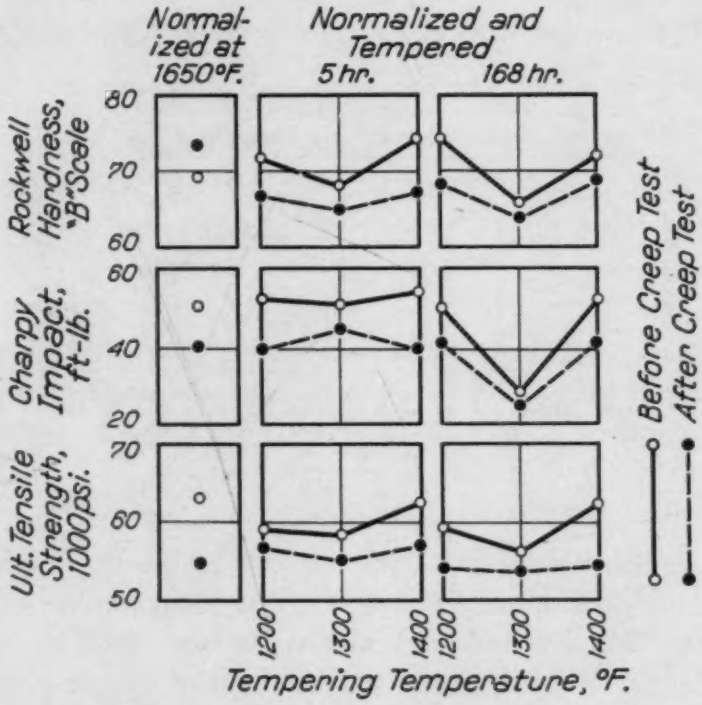


Fig. 6—Influence of Initial Heat Treatment and of Creep Testing at 1100 Degrees Fahr. on the Mechanical Properties of 0.11 Per Cent Carbon, 0.54 Per Cent Molybdenum Steel.

chart at × 100, and examination of the final microstructures shows no appreciable change in the grain size.

The difference in behavior of the pearlitic carbides and the groundmass precipitate suggests a difference in composition. The spheroidization and migration to the grain boundaries and agglomeration of the so-called "pearlitic" carbides bears a close similarity to the behavior of cementite in straight iron-carbon alloys, and this

material is probably an iron-rich molybdenum carbide. On the other hand, the groundmass precipitate forms slowly in fine particles in the ferrite and agglomerates *in situ*. While the composition of this fine precipitate is not definitely known, its appearance and behavior suggests that it is a molybdenum-rich carbide or possibly an iron-molybdenum intermetallic compound. The stability of such a precipitate probably accounts for its lasting ability to improve the creep resistance of the steel, as was suggested by E. C. Bain (5) in 1934.

Fig. 6 summarizes the influence of the original heat treatments and of time at temperature under stress on the mechanical properties of the carbon-molybdenum steel. The hardness of the initial normalized "A" material is somewhat raised by all of the heat treatments, except by spheroidizing at 1300 degrees Fahr. ("D" and "E" treatments); the impact strength is not appreciably altered except by

Table II
Divergence Between Linear and Parabolic Creep Rates

Heat Treatment	Divergence at, pounds per square inch							
	1500	2000	2500	3000	3500	4000	4500	5000
A	0	0	*0*	0.17	0.26	0.33	*0.57*	*1.00*
B	0	0	*0*	0	*0*	0.40	1.00	*1.70*
C	0	0	*0*	0	*0*	0.30	0.77	*1.65*
D	0	0	*0*	0	*0*	0	0.30	*0.49*
E	0	0	*0*	*0*	*0*	0.15	0.80	*2.05*
H	*—0.35*	—0.20	*0*	0.25	0.60	1.10	1.80	*2.55*
M	*0*	0	*0*	0	*0.30*	0.50	0.85	1.00

Divergence between linear and parabolic creep rates at 3000 hours, for specimens of carbon-molybdenum steel, expressed in millionths in./in./hr. The italicized values represent actual measurements. The remaining values were derived by interpolation from plotted curves, and are inserted to complete the description of the behavior of the specimens.

tempering for one week at 1300 degrees Fahr. ("E" treatment), which causes a considerable reduction, and the ultimate strength of the normalized material is somewhat lowered by all of the heat treatments, while the ductility as measured by the tensile elongation is practically unchanged. The influence of time at temperature under stress is to lower the room temperature strength as indicated by the hardness (except in "A" and "M"), tensile, and impact tests, and to slightly raise the ductility.

At the end of the test, it was found in general that the specimens had decreased about 2 per cent in diameter (4 per cent in cross sectional area) due to scaling. The consequent increase of stress was too small to alter the significance of the results. No decarburization or intergranular oxidation or cracking was evident at the surface of the specimens after the creep tests.

As mentioned under "Analysis of Observations," both the linear and the parabolic creep rate were calculated for each specimen. When these rates were plotted against the respective stresses, a set of curves was derived which showed the divergence between the two calculations. The divergence between these curves is summarized in Table II. A negative divergence indicates that the specimen tested at this stress had a decreasing (retarded) creep rate; a divergence of zero indicates a constant (linear) creep rate, and a positive divergence indicates an increasing (accelerated) creep rate. For any one initial heat treatment, successively higher stresses would probably have disclosed first a decreasing, then a constant, and finally an increasing creep rate. However, owing to the loads chosen, all of the specimens showed either constant or increasing creep rates except one. This specimen, H3, was subjected to the lowest stress employed in the "H" series, and had a decreasing creep rate. Specimen H1, subjected to the next highest stress, showed a linear (constant) creep rate, and specimen H2, subjected to the highest stress, showed an increasing creep rate.

An interesting property of the "D" and "E" treatments is brought out by this type of analysis. Table II shows that the rate of creep remains constant (divergence = 0) in the "D" and "E" structures over a wider range of stress than in the other treatments, and the divergence between the linear and the parabolic formulae at higher stresses is less for "D" than for any other original structure. The differences are greater and occur earlier in those steels (A, H, and M) in which the greatest amount of structural change occurs. The inference is that "D" and "E" are more structurally stable and may be subjected to higher stresses without danger of encountering an increasing creep rate. Since for a given stress, the actual rate of creep in "D" is much lower than for "E", it is immediately evident that, for the temperature, stresses, and length of time investigated, the "D" treatment is the best.

No direct comparisons can be made between the results of the present tests and those obtained by other investigators because of the dissimilarity in heat treatment, testing temperature, length of time at temperature, and stress employed. The influence of different preliminary heat treatments on the creep of carbon-molybdenum steel at 1022 degrees Fahr. under a stress of 20,160 pounds per square inch was described by Jenkins, Tapsell, Mellor, and Johnson (6). The minimum creep rate of a spheroidized steel was found to be 67.5

Table III

Results of Tests on Chromium-Molybdenum-Silicon Steel

Spec. No.	Temp. of Test °F	Creep Stress PSI	Duration of Creep Test Hrs.	Total Elong. Per Cent	Least Square Creep Rate at 3000 hours millionths in./in./hr.	Graphical Creep Rate during last 1000 hours millionths in./in./hr.	Diff. between Graph. and L. S. Creep Rates	Hard. Rock. B	Ultimate Tensile Strength PSI	Per Cent Elong. in 2"	Per Cent Reduction of Area	Impact Strength ft. lbs.
			Original Material									
C8-A	Room							84.2	82,220	28.0	71.5	43.5
C8-1	850	24,000	3,600	0.065	0.06	0.19	0.13	86.8	.....	...	...	43.5
C8-2	850	28,000	10,020	0.150	0.09*	0.13	0.04	89 0	.....	...	...	42.5
C8-3	850	32,000	2,420	....	0.13	0.12	0.01	84.2	.....	...	...	38.0
C8-8	950	15,000	3,000	0.156	0.49	0.52	0.03	...	75,900	30.0	73.1	...
C8-9	950	20,000	3,000	0.491	1.33	1.32	0.01	87.9	.....	...	...	34.5
C8-6	1,100	2,500	3,120	0.154	0.38	0.36	0.02	...	77,500	28.5	70.9	...
C8-4	1,100	5,000	3,000	0.347	0.79	0.67	0.12	88.3	.....	...	...	33.0
C8-5	1,100	6,000	3,130	0.381	0.83	0.67	0.16	...	72,000	24.0	71.8	...
C8-7	1,100	8,000	3,000	0.956	2.48	2.21	0.27	81.5	.....	...	...	39.0
C8-11**	1,100	6,000	2,230	....	0.66	0.65	0.01	78.8	.....	...	...	37.5

*Same at 10,000 hours.

**Special Heat Treatment (annealing).

millionths in./in./hr., 80 times that of an oil-quenched and tempered specimen. Creep data compiled by a subcommittee of the A.S.T.M. (7) contain references to short-time tests on carbon-molybdenum steel at 1000 and 1200 degrees Fahr.

Chromium-Molybdenum-Silicon Steel

The chromium-molybdenum-silicon steel employed in this investigation was made commercially in an electric furnace. Its composition was 0.20 per cent carbon, 0.49 per cent manganese, 0.019 per cent phosphorus, 0.009 per cent sulphur, 0.49 per cent silicon, 0.65 per cent molybdenum, and 1.56 per cent chromium. The standard heat treatment used for all the specimens before creep testing was: 1½ hours, 1750 degrees Fahr., air cool to 400 degrees Fahr., temper for 2 hours at 1375 degrees Fahr., furnace cool to 1000 degrees Fahr. and air cool to room temperature. A photomicrograph of this steel before creep testing is shown in Fig. 7. The hardness, impact strength, and tensile properties of the original material are given in Table III.

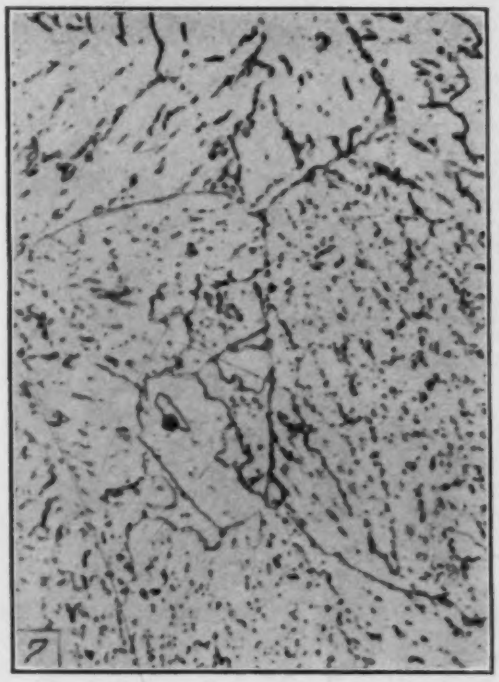


Fig. 7—Initial Structure of Chromium-Molybdenum-Silicon Steel before Creep Testing. × 1000.

Creep tests were conducted on this steel at 850, 950, and 1100

degrees Fahr. The rate of creep in the different specimens was analyzed by graphical and least square methods, as was described for the carbon-molybdenum steel. The differences between the rates computed by graphical and least square analysis are shown in Column 8, Table III. The stresses for a creep rate at 3000 hours of 1.0 millionths in./in./hr. at 950 and 1100 degrees Fahr. were respectively 19,750 and 6,250 pounds per square inch. These stresses were derived

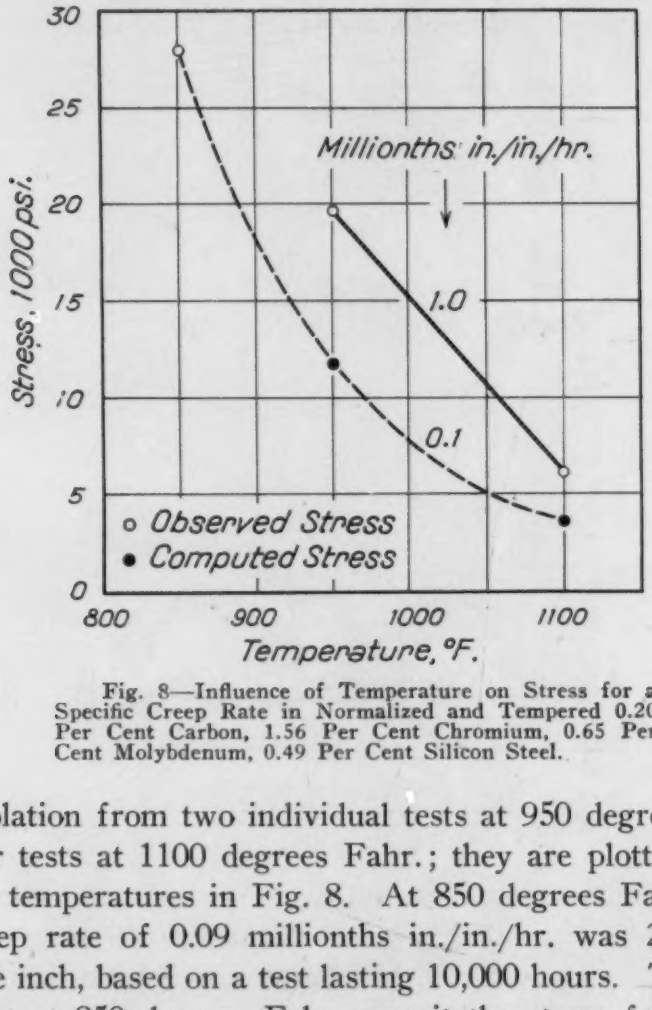


Fig. 8—Influence of Temperature on Stress for a Specific Creep Rate in Normalized and Tempered 0.20 Per Cent Carbon, 1.56 Per Cent Chromium, 0.65 Per Cent Molybdenum, 0.49 Per Cent Silicon Steel.

by interpolation from two individual tests at 950 degrees Fahr., and from four tests at 1100 degrees Fahr.; they are plotted against the respective temperatures in Fig. 8. At 850 degrees Fahr., the stress for a creep rate of 0.09 millionths in./in./hr. was 28,000 pounds per square inch, based on a test lasting 10,000 hours. The three tests carried out at 850 degrees Fahr. permit the stress for a creep rate of 0.1 millionths in./in./hr. to be derived by interpolation. Assuming as a first approximation that the stress for a creep rate of 0.1 millionths in./in./hr. is 60 per cent of the stress for a creep rate of 1.0 millionths in./in./hr., additional points are obtained for 950 and 1100 degrees Fahr., and the dotted curve is drawn on Fig. 8 to show the change of stress with temperature for a creep rate of 0.1 millionths in./in./hr.

The final structure of the specimens tested at 850 and 950 degrees Fahr. shows no certain differences from the initial material (Fig. 7), but at 1100 degrees Fahr., the period at temperature under stress promotes some spheroidization and coarsening of the carbides, and there is an indication of the development of a carbide network.

The final hardness, impact strength, and tensile properties of the specimens are listed in Table III. The influence of time at temperature under stress seemed to be to decrease the tensile and impact strength and slightly to increase the hardness.

In order to determine the influence of a different heat treatment on the creep properties of the chromium-molybdenum-silicon steel, a specimen was heat treated to produce a softer structure adapted to severe forming operations. Before creep testing it was held ½ hour at 1500 degrees Fahr. and then furnace-cooled at 50 degrees Fahr. per hour to 570 degrees Fahr., from which temperature it was air-cooled. This annealed specimen, tested at 1100 degrees Fahr. under a stress of 6000 pounds per square inch, had a creep rate of 0.66 millionths in./in./hr., somewhat lower than that (0.83 millionths in./in./hr.) produced by the same stress at the same temperature in the specimen which had been normalized and tempered.

Comparison of the results of the tests on chromium-molybdenum-silicon steel with those of other investigators encounters the same difficulties of dissimilarities in heat treatment and testing technique as were mentioned for carbon-molybdenum steel. A previous investigation (8) of annealed steel of the same type, but lower in chromium and carbon content, showed that a stress of 20,000 pounds per square inch was required for a creep rate of 0.1 millionths in./in./hr. at 800 degrees Fahr., and stresses of 24,000 and 6800 pounds per square inch for creep rates of 1.0 millionths in./in./hr. at 1000 and 1100 degrees Fahr. respectively. Another investigation (7) also showed results of tests on annealed steel of similar type at 800. 1000, and 1100 degrees Fahr. Creep rates of 0.2, 0.4, and 0.7 millionths in./in./hr. were reported as produced by stresses of 21,800, 17,500, and 6000 pounds per square inch at the respective temperatures. In comparison with these, the present tests indicate by interpolation stresses above 30,000, 8000, and 3000 pounds per square inch for a creep rate of 0.1 millionths in./in./hr. at 800, 1000, and 1100 degrees Fahr., and stresses of 14,000 and 6200 pounds per square inch for a creep rate of 1.0 millionths in./in./hr. at 1000 and 1100 degrees Fahr.

Conclusions

Least square analysis of creep data eliminates the personal error involved in graphical analysis, and permits a more certain evaluation of an increasing or a decreasing creep rate, thereby rendering somewhat less uncertain the values derived by extrapolation to longer periods. Within the time and temperature ranges investigated, successively higher stresses tend to produce first a decreasing, then a constant, and finally an increasing creep rate.

Specimens of carbon-molybdenum steel subjected to different heat treatments were found to possess widely different creep properties, which were definitely associated with changes in the microstructure. A creep rate of 1.0 millionths in./in./hr. was produced in the different specimens by stresses varying from 2300 to 3500 pounds per square inch, depending on the initial heat treatment. Of the seven heat treatments investigated, the maximum creep resistance over the 3000-hour test period was developed by the "D" treatment (tempering the normalized steel for five hours at 1300 degrees Fahr.), which produced a fine groundmass precipitate, probably a molybdenum-rich carbide. The stability of this precipitate probably accounts for its lasting ability to improve the creep resistance of the alloy. The structure produced by the "D" treatment maintained a constant (linear) creep rate at higher stresses than did the structures resulting from the other treatments, and the tendency to an increasing (accelerated) creep rate at higher stresses seemed to be least for this treatment, and maximum for those specimens showing the greatest changes in microstucture during the creep test. The behavior of the precipitate as demonstrated by the changes in microstructure offers a tangible reason for the improvement in creep resistance imparted to steel by the addition of molybdenum.

Creep tests on a normalized and tempered chromium-molybdenum-silicon steel indicated that a stress of 28,500 pounds per square inch was required for a creep rate of 0.13 millionths in./in./hr. at a temperature of 850 degrees Fahr. At 950 and 1100 degrees Fahr. stresses of 19,750 and 6250 pounds per square inch were required for a creep rate of 1.0 millionths in./in./hr. Annealed chromium-molybdenum-silicon steel was found to possess slightly greater creep resistance at 1100 degrees Fahr. than the same material which had been normalized and tempered.

The tensile, hardness, and impact properties of the carbon-molybdenum and chromium-molybdenum-silicon steel were somewhat

altered by time at temperature under stress toward lower strength and slightly higher ductility. In many cases, the changes in the mechanical properties could be related to corresponding changes in the microstructure.

Acknowledgments

The authors wish to express their indebtedness to E. L. Roff and Q. Henderson for their part in developing the equipment; to J. W. Bain and W. G. Benz for their assistance in carrying out the tests, and to H. Habart of the National Tube Company for his co-operation in preparing the specimens.

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DISCUSSION

Written Discussion: By C. L. Clark, Department of Engineering Research, University of Michigan, Ann Arbor, Mich.

The authors are to be congratulated on the great pains they have taken to demonstrate the influence of heat treatment on the resulting creep characteristics of two steels at certain temperatures. Their work is of special value in indicating the inadvisability of drawing too general conclusions with respect to certain of the factors influencing creep. For example, the general claim has often been made that spheroidization decreases the creep resistance. Their work indicates that such is not necessarily true. Their results also lend support to the statement many of us have made to the effect that the term spheroidization in itself is meaningless unless the degree of spheroidization is stated.

In regard to the statement appearing on page 93, I believe it will be found that stress exerts a rather pronounced influence on the observed structural changes. At least this was found to be true in the spheroidization studies which were conducted in our laboratories on several different steels.

Written Discussion: By R. W. Moore, General Laboratories, Socony-Vacuum Oil Co., Inc., Brooklyn, N. Y.

The authors are to be congratulated for this paper because it represents in our opinion, a step in the right direction in creep testing. It has been a matter of common knowledge that the examination of failed and used cracking still tubes of the low carbon and carbon-molybdenum type has revealed very marked changes in the microstructure and physical properties of the metal. The changes in physical properties of the metal after use have been, in our experience, a reduction in the hardness and tensile properties and an increase in ductility. These changes in the microstructure and physical properties have caused some speculation as to what the creep rates upon metal would be when it had reached or approached a state of stable equilibrium for its service temperature. The authors' conclusion that structural stability is accompanied by a constant creep rate is enlightening in this respect. Creep data on metal which has been structurally stabilized for the temperature for which it is to be used should be of more value to the designer than that obtained on metal in the normalized condition.

It should be pointed out also that the ultimate stable condition of the microstructure is obviously something which will vary with different furnaces and conditions of service. In the case of plain carbon steel there are conditions under which the carbides break down completely to graphite and iron. There are others where only a highly spheroidized condition is obtained. We have observed no cases of graphitization in low carbon steel tubes containing 0.5 per cent molybdenum. Many other peculiarities of structure have, however, been observed. It would be very difficult to reproduce these structures in steel in the laboratory in order to prepare test pieces which would be comparable to the condition obtained in service. This fact, of course, introduces a variable which is somewhat of a barrier to the exact interpretation of the creep data in actual practice. The changes in microstructure which take place in a creep test piece are not always the same as those obtained in the tubes in service. Certain changes in the microstructure of the steel can be made to take place in the laboratory or steel mill which no doubt approach those obtained in actual service. This is what the present authors have tried to do and it is for this reason that the work is a valuable contribution.

Oral Discussion

H. W. McQuaid:[1] The thing that interested me about it was the stable carbide; the effect of silicon on stabilizing the carbide in the ferrite below the critical range is, at least in my observation, quite marked. I was wondering if the difference in the two types of steel—the explanation of the difference in their properties—was not due to the difference in the stability of the carbide in the ferrite. The tendency in the first steel seemed to be to coalesce and precipi-

[1]Metallurgist, Republic Steel Corporation, Cleveland.

tate without any respect to the boundaries, whereas in the second steel, the chromium-silicon type, the carbides seemed to be very stable. I was wondering whether the first steel might not have had some aluminum in it?

J. J. KANTER:[2] The authors of the paper we have just heard are to be highly complimented for the very thorough manner in which they have studied the structural changes accompanying the creep of carbon-molybdenum steel. Their finding affords us much food for thought. Studies upon the particular aspect of creep which they have tackled are as yet too new to warrant any general conclusion. Indications are, however, in view of such results as the authors have just shown us, that all steels are structurally unstable at elevated temperature. No practical treatment can be accorded steels to render the carbides in perfect equilibrium at elevated temperatures, and it seems to be almost axiomatic that alterations of their phase and form will to some degree accompany long-time heating, whether or not stress be applied.

Experiments seem to indicate that stressing plays a minor role in the carbide changes which do take place, and that the effect on structure which we observe on microsections taken from creep test specimens are largely incidental to the heat to which they were subjected. Microstructures, studied after creep test exposure, therefore, while very important and of great desirability for the interpretation of results, reveal but little as to the mechanism of creep deformation, itself. It is to be hoped that future creep investigation will make use of additional tools which may throw more light upon the structural origin of creep strain under conditions where the phases are relatively stable in form and concentration. One of the possible tools which will aid toward this end is the use of creep test ovens in which chemically inert atmospheres can be maintained over an indefinite period. Such ovens will enable one to observe the effects of creep strain upon the surface structures of the test specimens. It will be possible in such equipment to directly observe the formation of slip lines, grain boundary features, and incipient cracks, directly upon the surface of the test specimens. After a suitable controlled atmosphere oven technique is developed, it will be but a short step to turn other tools of investigation than the microscope upon the surface of metal in process of creeping.

The authors extend a strong brief in behalf of computing their creep rates from least square determination of the creep-time curves. Such a proceeding is a mathematical nicety which is quite time consuming; many people question whether enough is gained thereby to warrant the expenditure of effort. Usually a line or curve can be drawn through the scatter of actual determinations well within the experimental certainty of any assumed curve. Least square analysis makes an a priori assumption that the creep strain versus time function is known and then it proceeds to determine the most probable values for this function which the data indicate.

Actually we have reason to believe that the creep strain versus time function is quite complex in view of the structural changes accompanying it. To compute the most probable straight line or parabola through an array of data is an assertion that the creep has taken place in accordance with either one law or the other, and quite an arbitrary choice is necessary in deciding which one to

[2]Research metallurgist, Crane Co., Chicago.

compute. It would seem that one could just as readily conform a draftsman's curve to the usual data, conforming much better to the average locus of the points, with greater reliability than is possible for the arbitrary choice between a straight line or a parabola bearing no physical interpretation with regard to the data.

Authors' Closure

In the discussion, Dr. Clark indicated his belief that stress exerts a rather pronounced influence on structural changes. It is our impression, gathered from the work of Dr. Clark and others, that high stress does promote structural change, provided that the temperature is sufficiently high, and that the higher the stress, the more pronounced is this phenomenon. Conversely, the lower the stress, the less its influence on structural changes, and the more the changes are to be ascribed to the influence of time at temperature. In this carbon-molybdenum steel at 1100 degrees Fahr., the structural changes were evidently due primarily to time at temperature, as the stress (from 1500 to 5000 pounds per square inch was too low to affect the structure appreciably. As stated on page 93, specimens of carbon-molybdenum steel were held under no stress at 1100 degrees Fahr. for successively longer time intervals up to 3000 hours; the dimensional changes were negligible. The specimen held 3000 hours was quite similar to the creep specimen held for the same length of time under a stress of 5000 pounds per square inch. Incipient spheroidization of the pearlite areas and faint traces of the background precipitate could be detected after 50 hours at 1100 degrees Fahr.; after 500 hours the majority of the structural changes were already quite apparent. The most pronounced change between 500 and 3000 hours exposure was coalescence of the spheroidized cementite with partial migration to the grain boundaries.

In regard to Dr. Moore's remarks, it should be pointed out that to stabilize a metal for the temperature at which it is to be used does not necessarily mean putting it in the form having the fastest creep rate at that temperature. The structure may be quite stable and yet its phases may be so finely distributed (as in the original "D" structure), that the metal shows excellent creep resistance.

In reply to Mr. McQuaid's inquiry as to the effect of silicon in stabilizing the carbide, we would call attention to the fact that the steel with the higher silicon also carried 1½ per cent chromium, which was absent in the carbon-molybdenum steel. We feel hardly warranted in ascribing any appreciable influence to silicon, at least so far as our data go, until other evidence is available on a similar steel containing approximately ½ per cent silicon without chromium. In the absence of an element, such as chromium or molybdenum, which forms a stable carbide, it is well known that silicon tends to promote graphitization; consequently, it seems somewhat unlikely that silicon alone would stabilize these carbides. Both steels referred to in this paper were killed with silicon and aluminum.

As Mr. Kanter points out, it is quite true that very little is known of the mechanism of creep deformation. Our purpose was simply to examine, in a single steel, the possible variation in creep behavior caused by variation of heat

treatment. The problem of the mechanism of deformation is a separate subject, and one well worth the difficult experimental technique which would be necessary.

With respect to the least square analysis of creep data, it will be seen from Tables I and III that the difference between the result of graphical and least square analysis is not significant when the creep rate is approximately constant over the period, but when the creep rate is not constant, graphical analysis is inadequate and may be inaccurate. In this case, the creep rate can only be expressed as the instantaneous slope of the curve at a given time; such an instantaneous rate is most readily obtained by means of least square analysis. As is pointed out in the text, least square analysis also eliminates personal error, and permits a smaller acceleration to be detected reliably than is feasible by graphical analysis. We have no evidence that creep curves are as complex as Mr. Kanter infers; they all show the familiar three stages, each stage being more or less pronounced, depending on the composition and prior treatment of the steel, the temperature, the stress, and the period of exposure.

The authors wish to express their appreciation for the interesting comments made in discussion of their paper.

RELATION OF PRE-TREATMENT OF STEELS TO AUSTENITIC GRAIN GROWTH

By J. E. Dorn and O. E. Harder

Abstract

This paper postulates that aluminum killed steels contain a grain growth inhibitor, the solubility of which in ferrite and in austenite increases with increase in temperature and that at the higher temperature range of ferrite the solubility is greater than at the low temperature range of austenite.

On the basis of this hypothesis a possible mechanism is suggested for the relation of pre-treatment of steels to the austenite grain growth. This hypothesis was tested first by heating steels at temperatures below the critical range; in one case just below the critical range to produce the maximum solubility of the grain growth inhibiting material in ferrite and in the other case, first, at a relatively high temperature and then for longer periods of time at lower temperatures to effect a lower solubility of the inhibitor in the ferrite. In general, the steels which were saturated with the grain growth inhibitor at temperatures just below the critical showed a higher coarsening temperature or less coarsening at a given temperature than those which were heat treated to give a lower amount of inhibitor in solution. Specimens which were heated directly from the saturation treatment or quenched and then rapidly reheated were more inclined to be fine grained than those which were slowly cooled from the saturation temperature and then reheated.

Specimens which were given a high temperature treatment in the austenite range to effect solution of the inhibitor and quenched, showed pronounced tendency to be fine-grained, whereas specimens with a similar treatment but slowly cooled tended to be coarse-grained. In a qualitative way the experimental results supported the mechanism postulated.

I. Introduction

PLAIN carbon steels having identical chemical compositions for the major components often exhibit different physical properties.

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. Of the authors, J. E. Dorn is research associate and O. E. Harder is assistant director, Battelle Memorial Institute, Columbus, Ohio. Manuscript received June 25, 1937.

Early investigations demonstrated that some of these differences were due to small additions of aluminum (and other metals) during the deoxidation process. Such additions are effective in modifying the growth characteristics of the austenite grains, and their influence on physical properties is, essentially, the result of this function.

The significance and importance of the austenite grain size to the physical properties of steels has been indicated in a rather recent symposium on austenite grain size (1).[1] The answers to two major questions, however, are still under discussion: 1. What chemical substances cause inhibited austenite grain growth? 2. By what mechanism is austenite grain growth inhibited? This paper discusses some aspects of the second of the above questions.

II. Austenite Formation and Grain Growth

A brief review of the essential differences between the austenite grain growth characteristics of unkilled and aluminum killed steels will illustrate what facts any theory of inhibited growth must explain.

Grossmann (3) demonstrated that austenite grains form at the cementite-ferrite interfaces of the pearlite patches. Such nuclei continue to assimilate the adjacent ferrite and cementite until the transformation is complete. The grain size developed at this time is called the initial austenite grain size. As shown by Herty, McBride, and Hough (6) the initial austenite grain size of unkilled steels is a function of the rate of passing through the transition range; as the rate increases the initial grains become coarser. Aluminum-killed steels were found, however, to develop small initial austenite grains independent of the rate of heating.

The austenite grains of unkilled steels continue to grow with time, even at temperatures just slightly above the transition temperature. The general mechanism of grain growth, as demonstrated by Davey (2), is applicable to this case. The arrangement of the atoms in the grain boundary is a compromise between the arrangement of the atoms in the adjacent grains; the grain boundary is a region of transition from the lattice orientation of one grain to that of the other. Due to thermal agitation, atoms in the grain boundary may align themselves in positions consistent with the symmetry of the grain having the lower free surface energy. The region

[1]The figures appearing in parentheses pertain to the bibliography appended to this paper.

of transition, the grain boundary, thus encroaches upon the grain having the higher free surface energy.

As Herty, McBride and Hollenback (5) have shown, aluminum killed steels maintain their initial austenite grain size for as long as forty-eight hours at the lower temperatures. As is generally known, however, when higher temperatures are employed a temperature at which grain growth begins will be reached. This is the minimum coarsening temperature. Only at and slightly above this tempera-

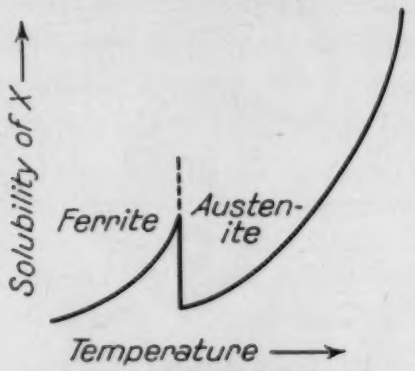

Fig. 1—Hypothetical Curve of Solubility of X in Ferrite and Austenite as a Function of Temperature.

ture have duplexed grain sizes been reported and this has also been observed in the present study. As still higher temperatures were employed uniformly coarse grains were obtained and, as has been previously reported, the grain size of aluminum killed steels was found to be even larger than that of similarly treated unkilled steels. Above the minimum coarsening temperature the austenite grains continue to grow with increased time. Grossmann (4) has shown that, in general, aluminum killed steels exhibit these peculiar growth characteristics and differ from unkilled steels and among themselves principally with respect to the actual temperature at which coarsening commences.

III. The Grain Boundary Precipitation Hypothesis for Inhibited Austenite Grain Growth

The product which causes inhibited austenite grain growth is commonly believed to be alumina. No direct proof of this, however, has been established. For this reason, the substance inhibiting the austenite grain growth of aluminum killed steels will be referred to as X, the unknown grain growth inhibitor.

As outlined in section II, any undissolved substance in the grain

boundary will inhibit grain growth. In order to account for the introduction of X in the grain boundary, the solubility curve shown in Fig. 1 is postulated. It is assumed that in both ferrite and austenite the solubility of X increases with increasing temperature. Since aluminum itself has a greater solubility in ferrite than in austenite it is logical to expect that the grain growth inhibitor, a compound of aluminum, will show the same trend. It is further assumed that X has a greater solubility in ferrite at the transition temperature than it has in the lower temperature regions of austenite. In the higher temperature regions of the austenite field, the solubility of X becomes greater than the maximum solubility in ferrite.

On the basis of the solubility curve of Fig. 1 there are several methods by means of which X may precipitate in the austenite grain boundary and prevent grain growth. Some of these will be illustrated in the following tests of the above postulate.

IV. A Preliminary Test of the Hypothesis

Commercial steels of the analyses given in Table I were employed in this investigation. They are placed in the order of decreasing coarsening tendency. Steels B 8 and B 6 were known to have had an aluminum addition and microscopic examination of inclusions and chemical analyses showed that steels B10, B12, and B9 were also aluminum-killed.

In a preliminary test of the grain boundary precipitation hypothesis, the thermal treatments outlined in Table II were performed. All samples were held at 2300 degrees Fahr. for 2 hours and cooled with the furnace to produce large austenite grains and also large ferrite grains and pearlite patches. Under these conditions any precipitation of X during cooling will be preferentially at the boundaries of the large austenite and large ferrite grains. Such a precipi-

Table I
Analyses of Commercial Steels*

Number	Per Cent						Aluminum Pound Per Ton
	Carbon	Manganese	Phosphorus	Sulphur	Silicon	Chromium	
B8	0.36	0.48	0.017	0.032	0.19	....	¾
B6	0.37	0.68	0.020	0.029	0.18	....	1
B10	0.41	0.81	0.022	0.024	0.14	0.11	(a)
B12	0.40	0.90	0.029	0.027	0.12	0.05	(a)
B9	0.35	0.80	0.022	0.024	0.07	0.06	(a)

*Analyses as reported by manufacturer.
(a) Microscopic examination and chemical analyses showed that these steels had also been killed with aluminum.

Table II
Heat Treatment to Test the Hypothesis

Sample	I. Held at 2300 Degrees Fahr. and Cooled with the Furnace	II. Aged at 1250 Degrees Fahr.	III. Aged at 1200 Degrees Fahr.	IV. Aged at 1000 Degrees Fahr.	V. Aged at 800 Degrees Fahr.	VI. Held at 1750 Degrees Fahr.
B8-H	2 hours	.....	15 hours	8 hours	42 hours	2 hours
B8-J	2 hours	25 hours	.....	.....	.....	2 hours
B6-H	2 hours	.....	15 hours	8 hours	42 hours	2 hours
B6-J	2 hours	25 hours	.....	.....	.....	2 hours
B10-H	2 hours	.....	15 hours	8 hours	42 hours	2 hours
B10-J	2 hours	25 hours	.....	.....	.....	2 hours
B12-H	2 hours	.....	15 hours	8 hours	42 hours	2 hours
B12-J	2 hours	25 hours	.....	.....	.....	2 hours
B9-H	2 hours	.....	15 hours	8 hours	42 hours	2 hours
B9-J	2 hours	25 hours	.....	.....	.....	2 hours

tate will have slight influence in retarding the growth of the future austenite grains. The series "J" was aged at 1250 degrees Fahr. for 25 hours in an attempt to produce a saturated solution of X in ferrite at this temperature. The series "H" was aged, as shown in Table II, in an attempt to produce a saturated solution of X in ferrite at 800 degrees Fahr. and to precipitate the excess X in the boundaries of the large ferrite grains. A longer time at 800 degrees Fahr. was employed because of the lower rate of diffusion at the lower temperature. The austenite grain size was then determined by taking the samples directly to 1750 degrees Fahr. (5 minutes) holding for 2 hours, and quenching after a short arrest at 1380 degrees Fahr.

The resulting austenite grain sizes are shown in Fig. 2. With reference to coarsening the following deductions were made. Samples B6-H, B10-H, and B12-H, which were aged at 1200, 1000, and 800 degrees Fahr., exhibited greater coarsening than B6-J, B10-J, and B12-J, which were aged at 1250 degrees Fahr. In other words the "J" samples of these steels had a higher coarsening temperature than the corresponding "H" samples. Both B8-H and B8-J coarsened equally. For B9-H and B9-J the coarsening temperature was not exceeded.

If the solubility of X increases with temperature, as suggested in Fig. 1, samples "J" should have a greater amount in solution than samples "H" after aging. Hence, when they are taken into the austenite field samples "J" should precipitate more X in the austenite grain boundaries than the corresponding samples "H." Consequently, samples "J" should have a higher coarsening temperature. This was observed for steels B6, B10, and B12.

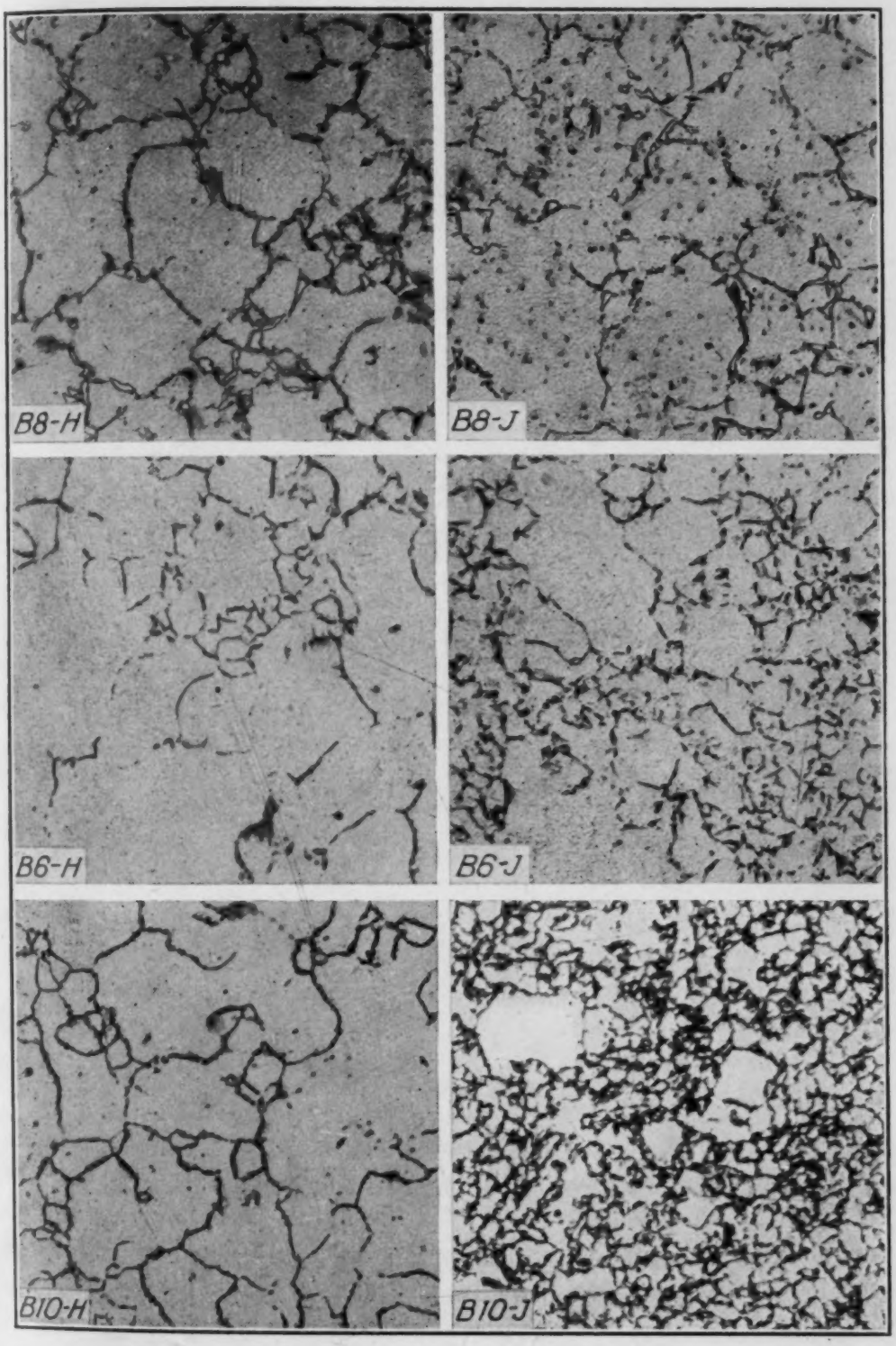

Fig. 2—The Influence of Subcritical Aging on the Coarsening Temperature of the Austenite Grains.

Series "H"

Held at 2300 degrees Fahr. for 2 hours and cooled with the furnace.

Aged at 1200 degrees Fahr. for 15 hours.

Aged at 1000 degrees Fahr. for 8 hours.

Series "J"

Held at 2300 degrees Fahr. for 2 hours and cooled with the furnace.

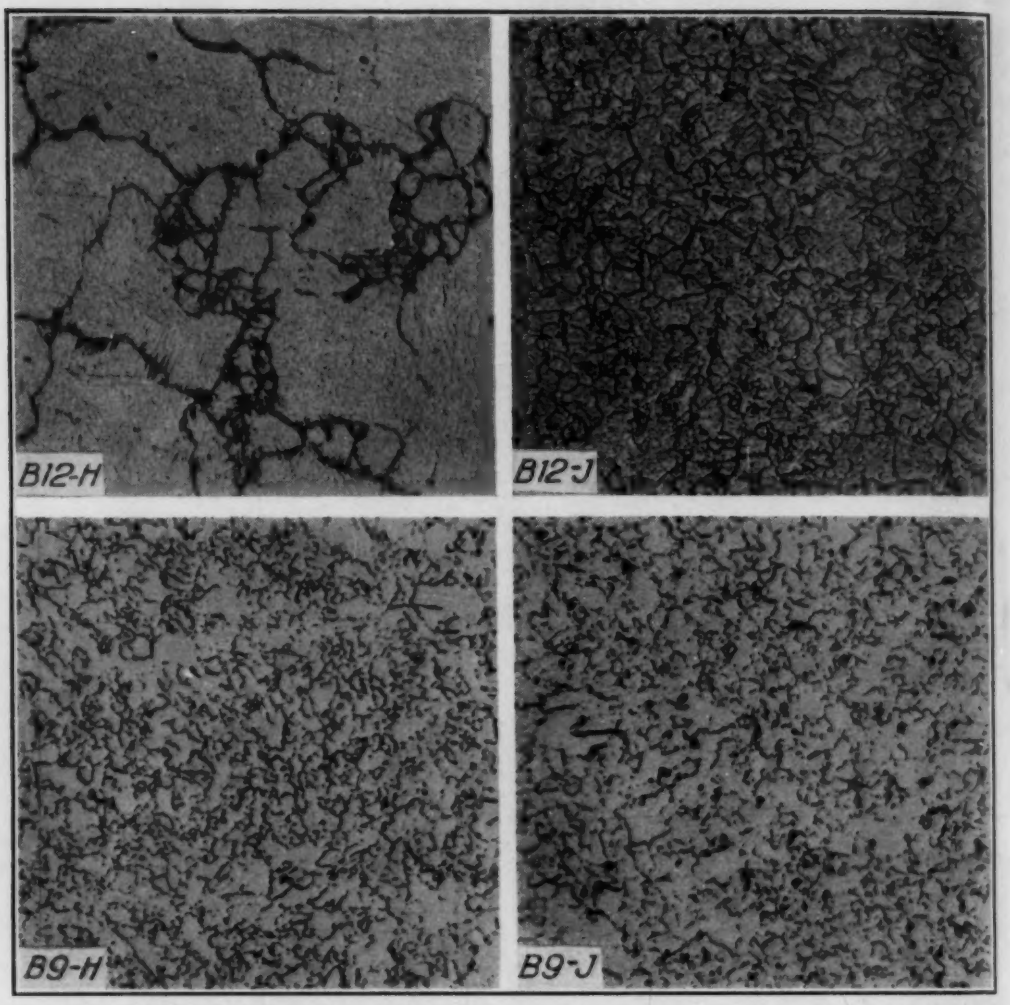

Fig. 2. Continued—The Influence of Subcritical Aging on the Coarsening Temperature of the Austenite Grains.

Series "H"—Continued
Aged at 800 degrees Fahr. for 42 hours.
Held at 1750 degrees Fahr. for 2 hours.
Arrested quenched.
Photomicrographs × 50.

Series "J"—Continued
Aged at 1250 degrees Fahr. for 25 hours.
Held at 1750 degrees Fahr. for 2 hours.
Arrested quenched.
Photomicrographs × 50.

Steel B8 has a very low coarsening temperature and therefore only a limited supply of X. It was found that even at 1550 degrees Fahr. steel B8 coarsened. Under these conditions it may be assumed that insufficient X for saturation was available. The results for B8 are, therefore, consistent with the postulate.

Since steel B9 has a high coarsening temperature, it was believed that the expected difference would appear at some higher temperature. At 1800 degrees Fahr. it was found that the sample of B9 aged at 1250 degrees Fahr. for 25 hours showed less coarsening

than the sample aged at 1200 degrees Fahr. for 15 hours, at 1000 degrees Fahr. for 8 hours and 800 degrees Fahr. for 42 hours.

These tests lead to the conclusion that (1) the solubility of X in ferrite increases with temperature and (2) at 1250 degrees Fahr. this solubility exceeds the solubility of X in austenite at the lower temperatures; (3) the excess X in solution in ferrite over the saturation value in austenite precipitates in boundaries of the newly formed austenite grains and prevents grain growth; (4) at the coarsening temperature the film of X dissolves at its thinnest points causing duplexed grain size; (5) above the coarsening temperature complete solution of this film takes place and uniform grain growth occurs.

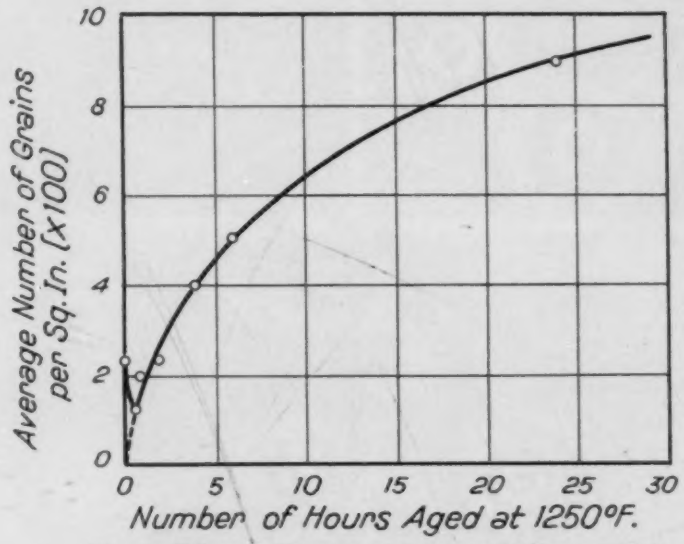

Fig. 3—Effect of Time of Aging at 1250 Degrees Fahr. Upon the Austenite Grain Size as Determined in 1 Hour at 1750 Degrees Fahr.

V. The Influence of Time of Aging on the Future Austenite Grain Size

It has been shown that the coarsening temperature of aluminum killed steels is affected by the previous subcritical heat treatment. An alteration in the coarsening temperature may also cause an alteration in the actual austenite grain size in a given thermal treatment. In order to investigate the effect of aging at 1250 degrees Fahr. on the future austenite grain size, the heat treatments given in Table III were performed.

As shown by the austenite grain size at 1750 degrees Fahr., with increasing time of aging at 1250 degrees Fahr., the grains become

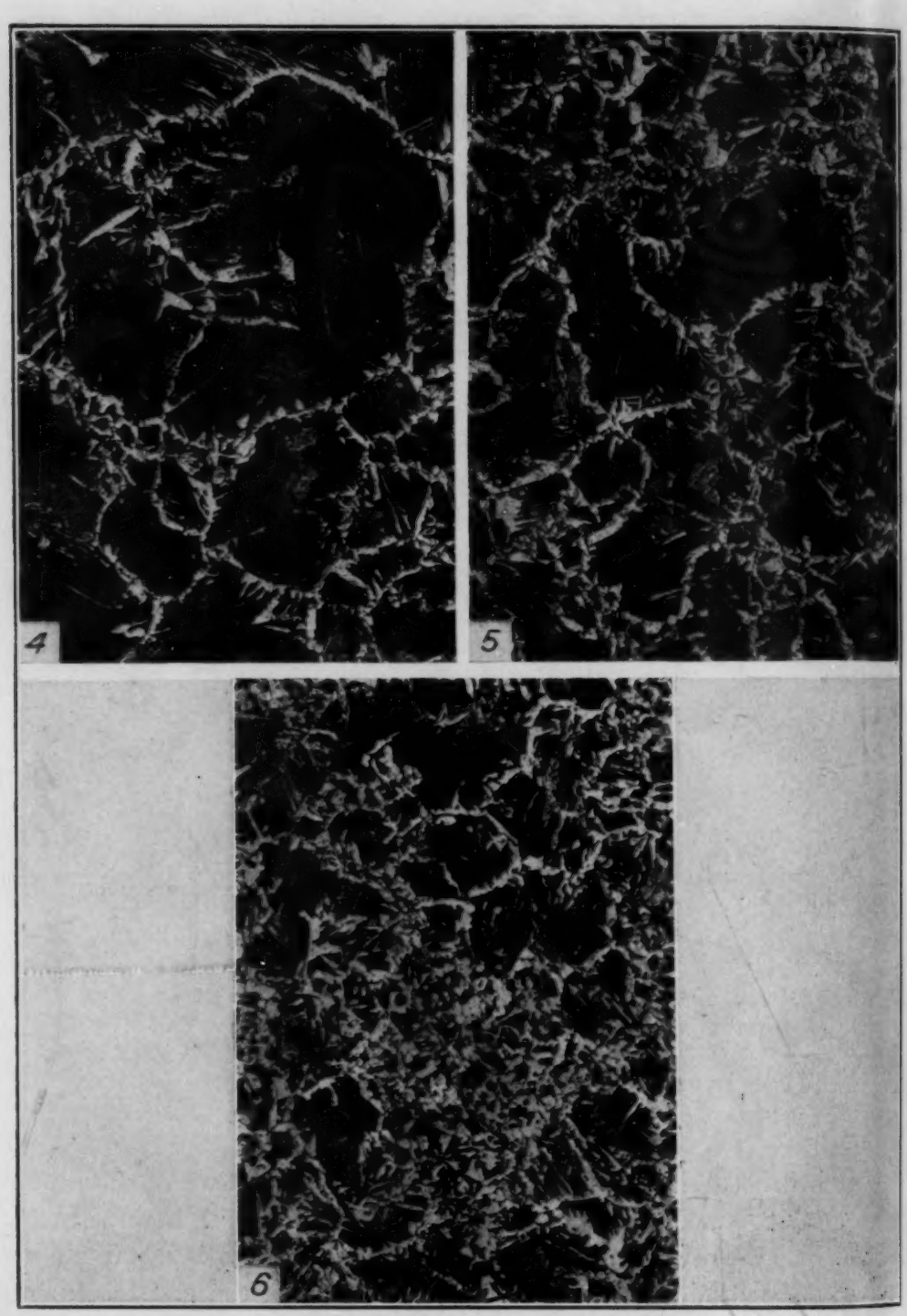

Fig. 4—B10-15. Heated to 2300 Degrees Fahr. for 2 Hours and Cooled With the Furnace. Aged at 1250 Degrees Fahr. for ½ Hour. Heated to 1750 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 5—B10-7. Heated to 2300 Degrees Fahr. for 2 Hours and Cooled With the Furnace. Aged at 1250 Degrees Fahr. for 6 Hours. Heated to 1750 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 6—B10-5. Heated to 2300 Degrees Fahr. for 2 Hours and Cooled With the Furnace. Aged at 1250 Degrees Fahr. for 24 Hours. Heated to 1750 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

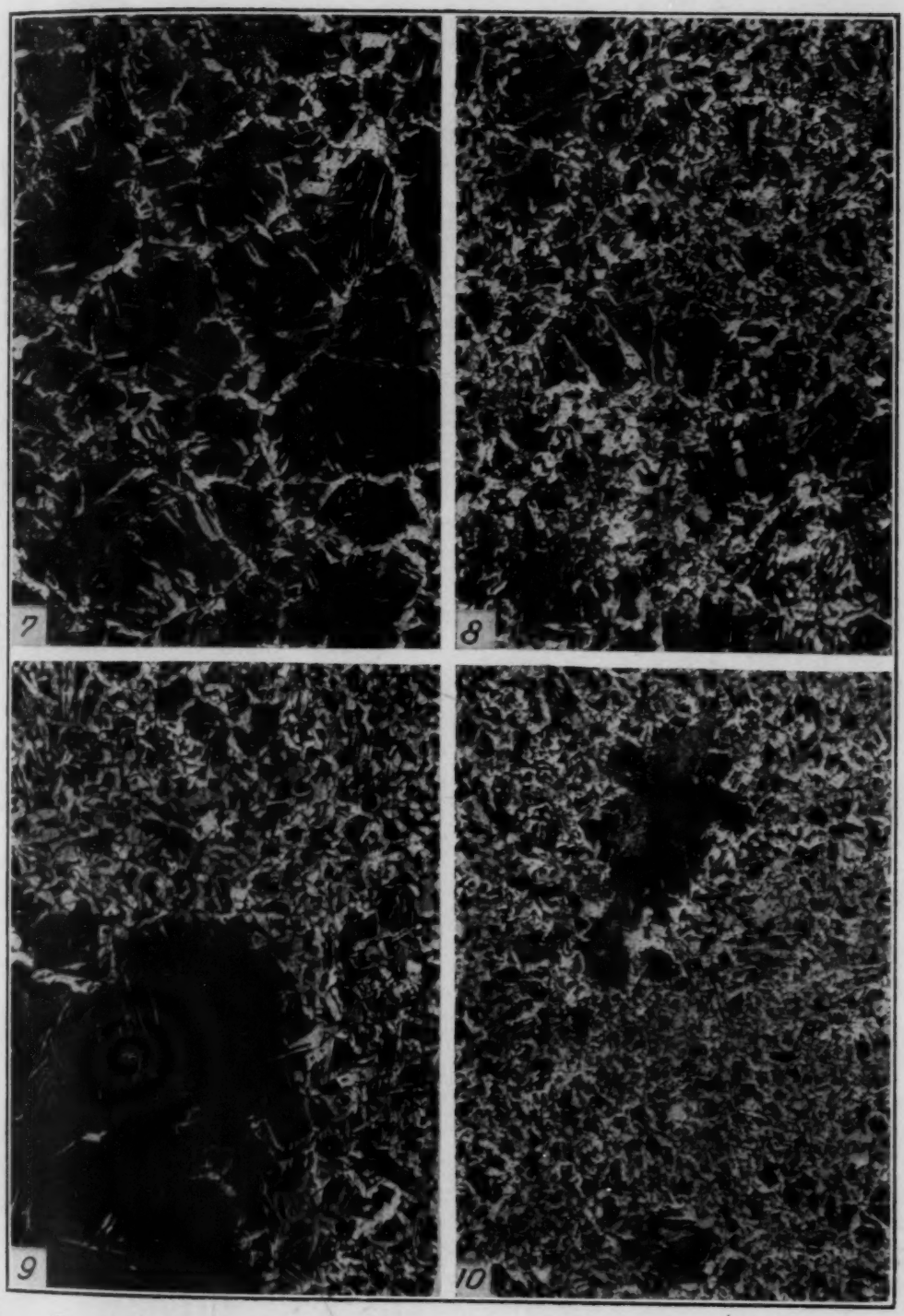

Fig. 7—B10-1. Heated to 1750 Degrees Fahr. 1 Hour and Rapidly Cooled. × 100.
Fig. 8—B10-3. Aged at 1250 Degrees Fahr. for 24 Hours. Heated to 1750 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.
Fig. 9—B10-18. Heated to 2300 Degrees Fahr. for 2 Hours and Cooled With the Furnace. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.
Fig. 10—B10-6. Heated to 2300 Degrees Fahr. for 2 Hours and Cooled With the Furnace. Aged at 1250 Degrees Fahr. for 24 Hours. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100

smaller. This trend is illustrated in Fig. 3. It is apparent, however, that even in 24 hours equilibrium between the dissolved and solid X has not been established. In other words, the process of solution and diffusion of X in ferrite at 1250 degrees Fahr. is extremely slow.

Photomicrographs of the specimens representing the ½, 6 and 24 hour points of the curve in Fig. 3 are shown in Figs. 4, 5, and 6, respectively. The change is quite pronounced. This method of pre-

Table III

Heat Treatment to Illustrate the Effect of Aging at 1250 Degrees Fahr. Upon the Austenite Grain Size as Determined at 1650 and 1750 Degrees Fahr.

Sample	Preliminary Treatment	Aged at 1250 Degrees Fahr.	One Hour at Temperature and Cooled Rapidly Degrees Fahr.	Number of Austenite Grains Per Sq. Inch (X100)
B10-5	2300 degrees Fahr. for 2 hours and slowly cooled	24 hours	1750	9. [1]
B10-7	2300 degrees Fahr. for 2 hours and slowly cooled	6 hours	1750	5.12
B10-9	2300 degrees Fahr. for 2 hours and slowly cooled	4 hours	1750	4.12
B10-11	2300 degrees Fahr. for 2 hours and slowly cooled	2 hours	1750	2.30
B10-13	2300 degrees Fahr. for 2 hours and slowly cooled	1 hour	1750	2.04
B10-15	2300 degrees Fahr. for 2 hours and slowly cooled	½ hour	1750	1.36
B10-17	2300 degrees Fahr. for 2 hours and slowly cooled	0 hour [2]	1750	2.32
B10-3	As received	24 hours	1750	...
B10-1	As received	0 hour [2]	1750	...
B10-6	2300 degrees Fahr. for 2 hours and slowly cooled	24 hours	1650	...
B10-8	2300 degrees Fahr. for 2 hours and slowly cooled	6 hours	1650	...
B10-10	2300 degrees Fahr. for 2 hours and slowly cooled	4 hours	1650	...
B10-12	2300 degrees Fahr. for 2 hours and slowly cooled	2 hours	1650	...
B10-14	2300 degrees Fahr. for 2 hours and slowly cooled	1 hour	1650	...
B10-16	2300 degrees Fahr. for 2 hours and slowly cooled	½ hour	1650	...
B10-18	2300 degrees Fahr. for 2 hours and slowly cooled	0 hour [2]	1650	...
B10-2	As received	24 hours	1650	...
B10-4	As received	0 hour [2]	1650	...

[1] Estimated value.
[2] Heated directly from room temperature.

treating for finer austenite grains may prove effective in reclaiming steels coarsened by overheating. Furthermore, the method may also be applied to steels in the as-received condition in order to retard or prevent the growth of the future austenite grain. This application is shown in Figs. 7 and 8, in which the specimen aged 24 hours at 1250 degrees Fahr. shows a finer grain.

When the austenite grain size is determined at 1650 degrees Fahr. the same trend is noted. Figs. 9 and 10 show the effect of

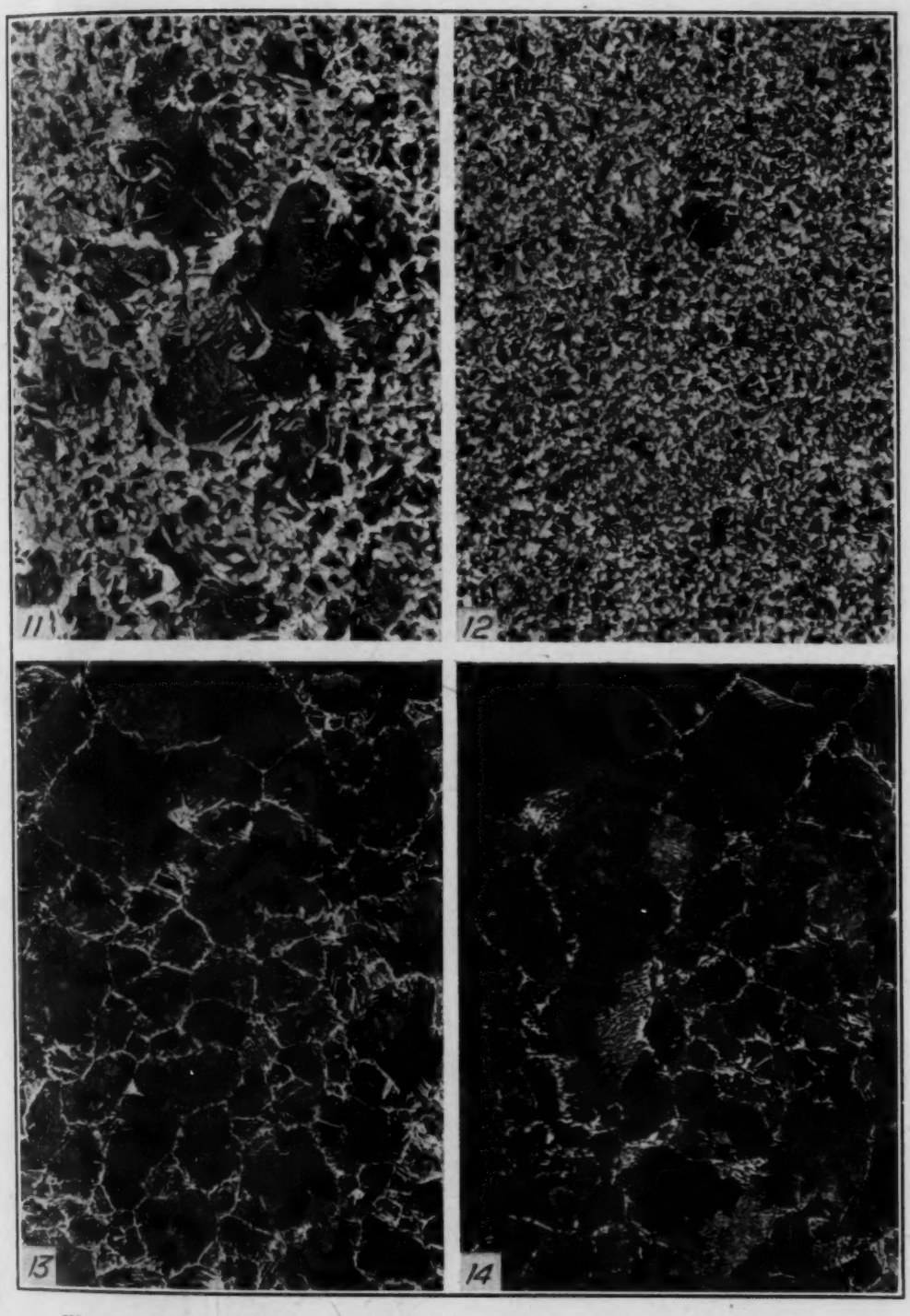

Fig. 11—B10-4. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 12—B10-2. Aged at 1250 Degrees Fahr. for 24 Hours. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 13—B10-24. Held at 2300 Degrees Fahr. for 2 Hours and Cooled With the Furnace. Aged at 1250 Degrees Fahr. for 24 Hours and Cooled 100 Degrees Fahr. Per Hour. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 14—B10-23. Held at 2300 Degrees Fahr. for 2 Hours and Cooled With the Furnace. Aged at 1250 Degrees Fahr. for 24 Hours and Cooled 25 Degrees Fahr. Per Hour. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

aging on an overheated sample and Figs. 11 and 12 show the effect of aging on as-received samples.

Aging some steels at 1250 degrees Fahr. raises the coarsening temperature of the austenite grains. This is believed to be due to a solution of X in ferrite during aging and its precipitation at the boundaries of the newly formed austenite grains during transition. Changes in the actual austenite grain size at a given temperature are believed to be results of changes in the coarsening temperature which, as has been shown in the preceding section, is influenced by aging at subcritical temperatures.

VI. The Influence of the Rate of Cooling from 1250 Degrees Fahr. on the Future Austenite Grain Size

In order to test the effect of the rate of cooling from 1250 degrees Fahr. on the future austenite grain size, the heat treatments given in Table IV were performed. The sample aged for 24 hours at 1250 degrees Fahr. are assumed to be practically saturated with X. The samples aged for ½ hour at 1250 degrees Fahr. are highly unsaturated.

B10-19, which was quenched in water, and B10-21, which was air cooled, were equally fine grained when heated for one hour at

Table IV

Heat Treatment to Test the Influence of the Rate of Cooling on the Future Austenite Grain Size

Sample	Preliminary Operation	Aged 1250 Degrees Fahr.	Rate of Cooling to Room Temperature	Heated For One Hour at Degrees Fahr.
B10-19	2300 degrees Fahr. for 2 hours and cooled with the furnace	24 hours	Quenched in H_2O	1650
B10-21	2300 degrees Fahr. for 2 hours and cooled with the furnace	24 hours	Air cooled	1650
B10-24	2300 degrees Fahr. for 2 hours and cooled with the furnace	24 hours	100°F./hour	1650
B10-23	2300 degrees Fahr. for 2 hours and cooled with the furnace	24 hours	25°F./hour	1650
B10-20	2300 degrees Fahr. for 2 hours and cooled with the furnace	24 hours	Quenched in H_2O	1750
B10-22	2300 degrees Fahr. for 2 hours and cooled with the furnace	24 hours	Air cooled	1750
B10-26	2300 degrees Fahr. for 2 hours and cooled with the furnace	24 hours	100°F./hour	1750
B10-25	2300 degrees Fahr. for 2 hours and cooled with the furnace	24 hours	25°F./hour	1750
B10-30	2300 degrees Fahr. for 2 hours and cooled with the furnace	½ hour	100°F./hour	1750
B10-29	2300 degrees Fahr. for 2 hours and cooled with the furnace	½ hour	25°F./hour	1750
B10-28	As received	24 hours	100°F./hour	1750
B10-27	As received	24 hours	25°F./hour	1750
B10-32	As received	½ hour	100°F./hour	1750
B10-31	As received	½ hour	25°F./hour	1750

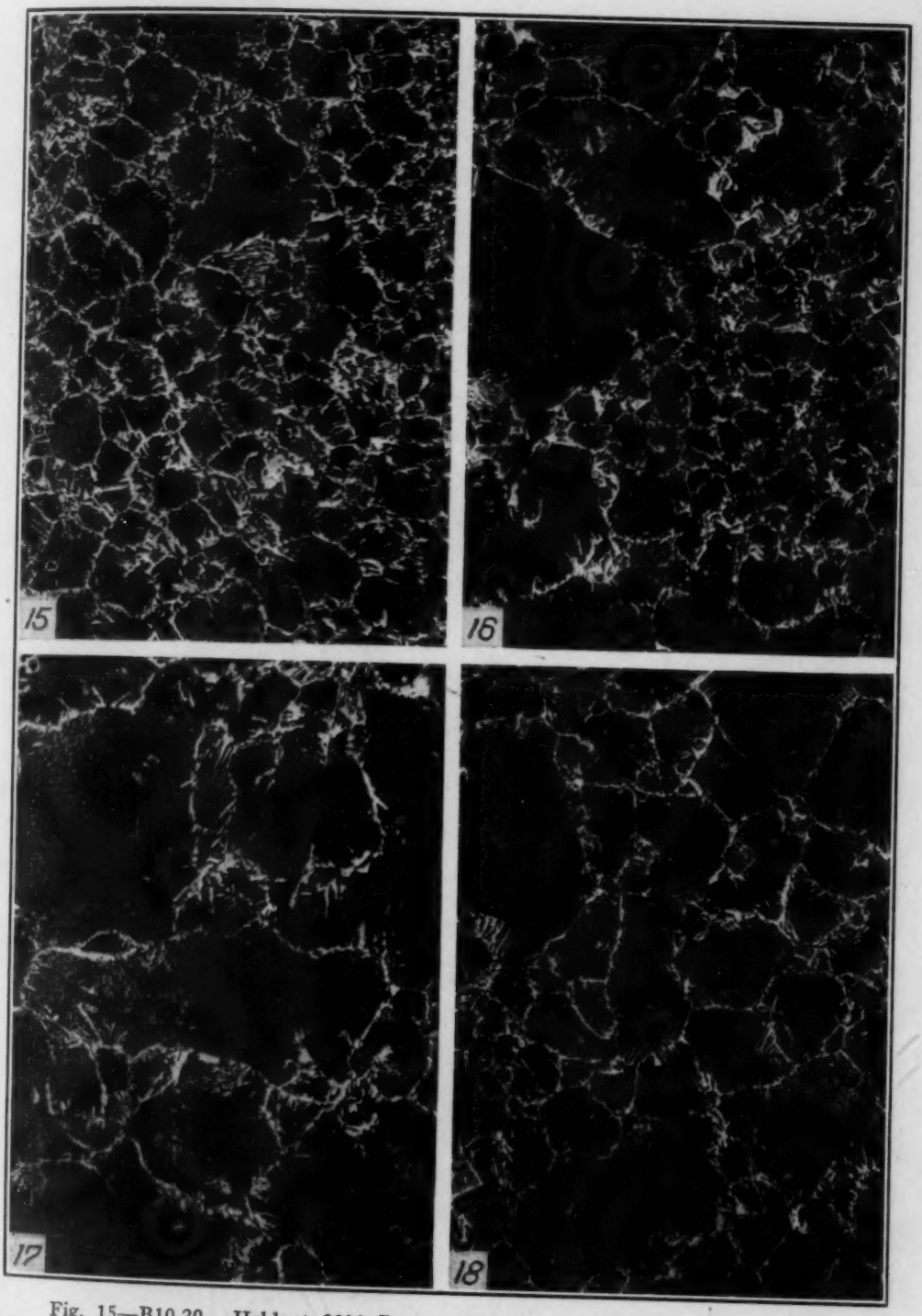

Fig. 15—B10-20. Held at 2300 Degrees Fahr. for 2 Hours and Cooled With the Furnace. Aged at 1250 Degrees Fahr. for 2 Hours and Quenched in Water. Heated to 1750 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 16—B10-22. Held at 2300 Degrees Fahr. for 2 Hours and Cooled With the Furnace. Aged at 1250 Degrees Fahr. for 24 Hours and Cooled in Air. Heated to 1750 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 17—B10-30. Held at 2300 Degrees Fahr. for 2 Hours and Cooled With the Furnace. Aged at 1250 Degrees Fahr. for ½ Hour and Cooled 100 Degrees. Fahr. Per Hour. Heated to 1750 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 18—B10-29. Held at 2300 Degrees Fahr. for 2 Hours and Cooled With the Furnace. Aged at 1250 Degrees Fahr. for ½ Hour and Cooled 25 Degrees Fahr. Per Hour. Heated to 1750 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

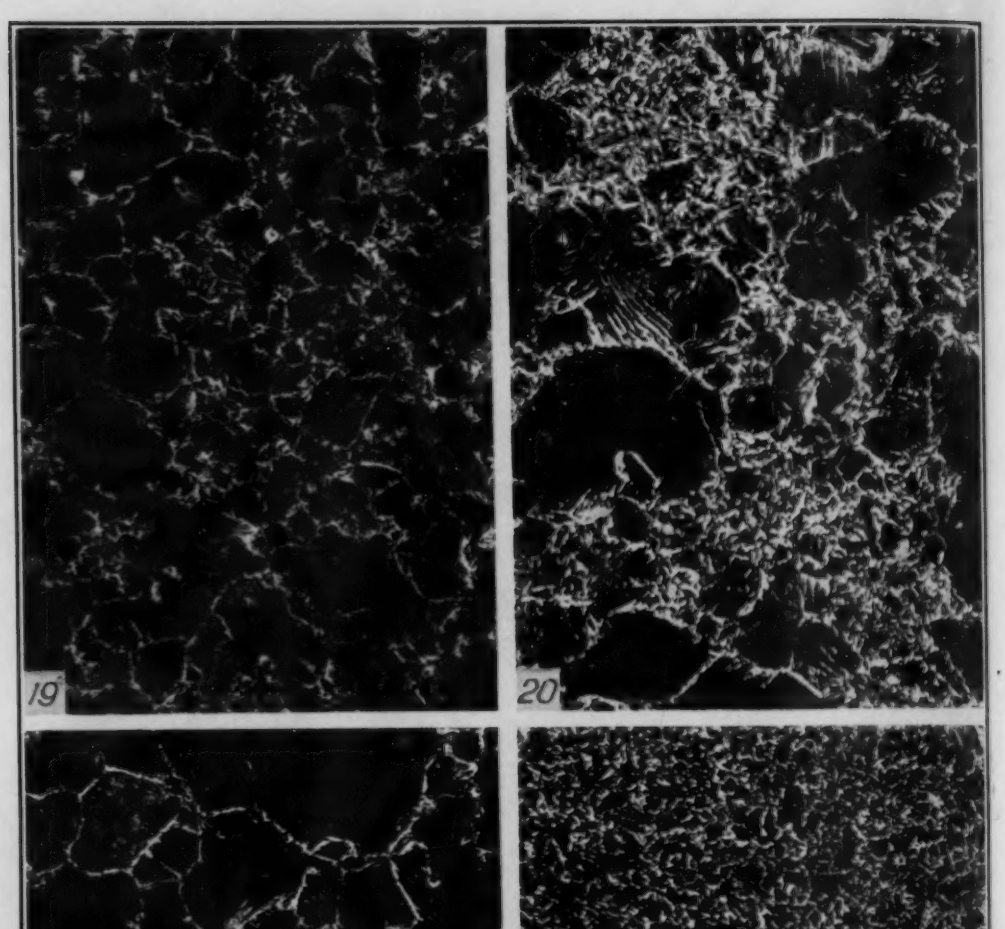

Fig. 19—B10-GB. Held at 2000 Degrees Fahr. for 1 Hour and Quenched in Water. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 20—B10-GD. Held at 2000 Degrees Fahr. for 1 Hour and Quenched in Water. Heated to 1500 Degrees Fahr. for 3 Hours and Quenched in Water. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 21—B10-EB. Held at 2000 Degrees Fahr. for 1 Hour and Cooled to 1500 Degrees Fahr. in 1½ Hours. Held at 1500 Degrees Fahr. for 3 Hours and Quenched in Water. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 22—B9-GB. Held at 2000 Degrees Fahr. for 1 Hour and Quenched in Water. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

1650 degrees Fahr. B10-24 (Fig. 13), which was cooled 100 degrees Fahr. per hour, was much coarser. B10-23 (Fig. 14), which was cooled 25 degrees Fahr. per hour, was slightly coarser than the sample cooled 100 degrees Fahr. per hour.

The same trend was observed when the austenite grain size at 1750 degrees Fahr. was investigated. Sample B10-20, (Fig. 15), which was quenched in water, was relatively fine grained. B10-22, (Fig. 16), which was air cooled, has a duplexed grain size with larger grains than those observed in the quenched specimen. B10-26, cooled 100 degrees Fahr. per hour, and B10-25, cooled 25 degrees Fahr. per hour, were both entirely coarse grained. The same result was observed for B10-28, and B10-27, which were not given the preliminary overheating. Furthermore, a comparison of Figs. 13 and 15 will show that the sample quenched in water has a finer austenite grain size at 1750 degrees Fahr. than the sample cooled 100 degrees Fahr. per hour has at 1650 degrees Fahr.

These results are entirely consistent with those anticipated on the basis of the solubility curve shown in Fig. 1. Aging at 1250 degrees Fahr. for 24 hours produces, for all practical purposes, a saturated solution of X at this temperature. As the samples are cooled, precipitation of X occurs and the quantity in solution diminishes. The samples which were rapidly cooled largely retain the dissolved X in the form of a metastable solution. Those samples which were cooled more slowly have less retained X in solution and approximate more closely the true saturation solubility at the lower temperatures. Therefore, the more slowly cooled samples precipitate less X in the boundaries of the newly formed austenite grains upon reheating and, consequently, have a lower coarsening temperature.

The samples aged for only ½ hour at 1250 degrees Fahr. are obviously unsaturated. With such samples, rapid rates of cooling prevent any pronounced precipitation or further solution. Slower rates of cooling favor solution at the higher temperatures. The processes of solution, precipitation, and diffusion are so slow at the lower temperatures that they are ineffective. Therefore the more slowly cooled unsaturated samples should have higher coarsening temperature and a correspondingly modified austenite grain size. This result was observed in the previously coarsened samples, B10-30 and B10-29, and also in the as-received samples B10-32 and B10-31. The differences noted in B10-30 and B10-29 may be seen by comparing the photomicrographs of Figs. 17 and 18.

The consistency of these results strengthens the contention that the solubility of X is quite similar to that illustrated in Fig. 1.

VII. The Influence of Quenching from the Austenite Field on the Future Austenite Grain Size

In order to test the influence of quenching from the austenite field on the future austenite grain size the heat treatments given in Table V were performed. Sample B10-GB (Fig. 19), which was quenched from 2000 degrees Fahr., was finer at 1650 degrees Fahr. than sample B10-GD (Fig. 20), which was quenched from 2000 degrees Fahr. and reheated to 1500 degrees Fahr. for 3 hours, requenched and then heated to 1650 degrees Fahr. for 1 hour. Sample B10-EB (Fig. 21), which was slowly cooled from 2000 degrees Fahr. to 1500 degrees Fahr. and quenched, showed a definitely coarsened austenite grain at 1650 degrees Fahr. The same trend was noted in samples B10-GA, B10-GC, and B10-EA, when the austenite grain size was determined at 1750 degrees Fahr.

Sample B9-GB (Fig. 22), which was quenched from 2000 degrees Fahr., exhibited a very fine austenite grain size when reheated to 1650 degrees Fahr. Approximately the same fine structure was found in B9-GD (Fig. 23), which was quenched from 2000 degrees Fahr. heated to 1500 degrees Fahr. for 3 hours, requenched and then

Table V

Heat Treatment to Test the Influence of Quenching from Austenite on the Future Austenite Grain Size

Sample	Operation I.	Operation II.	Operation III.	Operation IV.	Operation V.
B9-GA	2000°F. for one hour	Quenched in H_2O			1750°F. 1 hr.
B10-GA	2000°F. for one hour	Quenched in H_2O			1750°F. 1 hr.
B9-GB	2000°F. for one hour	Quenched in H_2O			1650°F. 1 hr.
B10-GB	2000°F. for one hour	Quenched in H_2O			1650°F. 1 hr.
B9-GC	2000°F. for one hour	Quenched in H_2O	1500°F. for 3 hours	Quenched in H_2O	1750°F. 1 hr.
B10-GC	2000°F. for one hour	Quenched in H_2O	1500°F. for 3 hours	Quenched in H_2O	1750°F. 1 hr.
B9-GD	2000°F. for one hour	Quenched in H_2O	1500°F. for 3 hours	Quenched in H_2O	1650°F. 1 hr.
B10-GD	2000°F. for one hour	Quenched in H_2O	1500°F. for 3 hours	Quenched in H_2O	1650°F. 1 hr.
B9-EA	2000°F. for one hour	Cooled 1½ hrs. to 1500°F.	1500°F. for 3 hours	Quenched in H_2O	1750°F. 1 hr.
B10-EA	2000°F. for one hour	Cooled 1½ hrs. to 1500°F.	1500°F. for 3 hours	Quenched in H_2O	1750°F. 1 hr.
B9-EB	2000°F. for one hour	Cooled 1½ hrs. to 1500°F.	1500°F. for 3 hours	Quenched in H_2O	1650°F. 1 hr.
B10-EB	2000°F. for one hour	Cooled 1½ hrs. to 1500°F.	1500°F. for 3 hours	Quenched in H_2O	1650°F. 1 hr.

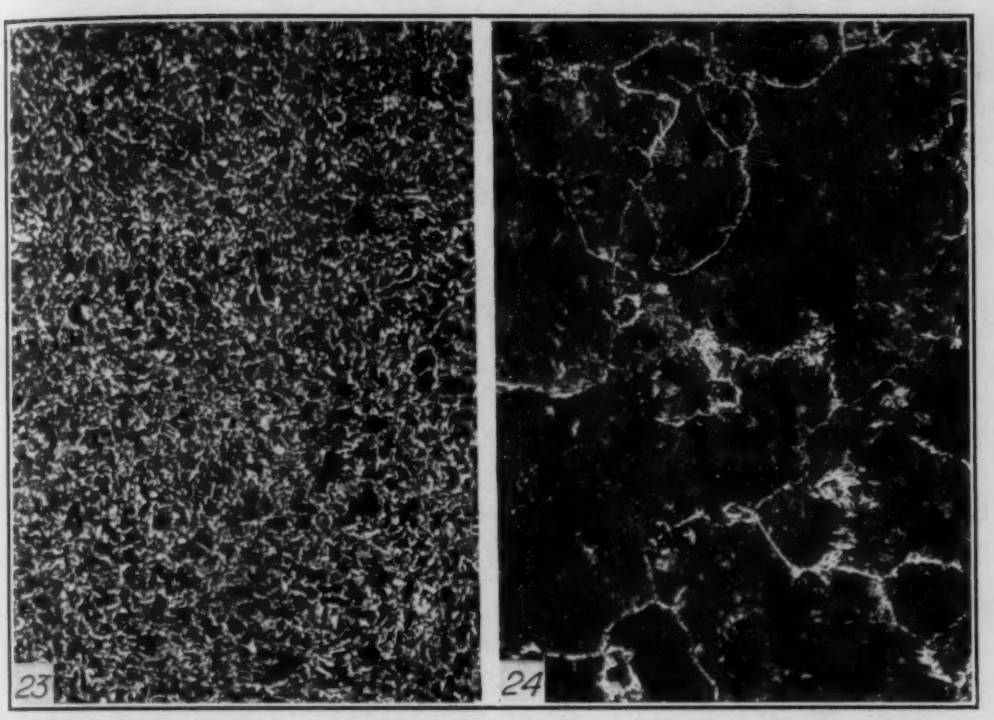

Fig. 23—B9-GD. Held at 2000 Degrees Fahr. for 1 Hour and Quenched in Water. Heated to 1500 Degrees Fahr. for 3 Hours and Quenched in Water. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 24—B9-EB. Held at 2000 Degrees Fahr. for 1 Hour and Cooled in 1½ Hours to 1500 Degrees Fahr. Held at 1500 Degrees Fahr. for 3 Hours and Quenched in Water. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

heated to 1650 degrees Fahr. for 1 hour. In contrast, however, sample B9-EB (Fig. 24), which was slowly cooled to 1500 degrees Fahr. and then quenched, developed very large austenite grains at 1650 degrees Fahr. Samples B9-GA, B9-GC, and B9-EA, which were similarly treated show the same trend when the austenite grains formed at 1750 degrees Fahr. are studied.

If the solubility of X in austenite increases with temperature as indicated in Fig. 1 a very large quantity should go into solution at 2000 degrees Fahr. Quenching from 2000 degrees Fahr. prevents, to a great extent, its diffusion and precipitation. When the steel is again heated into the austenite field a large quantity of X is precipitated in the boundaries of newly formed austenite grains. This elevates the coarsening temperature and consequently accounts for the fine austenite grains found in the samples which were quenched from 2000 degrees Fahr. and reheated.

As the samples were slowly cooled from 2000 to 1500 degrees Fahr. the X precipitated in the boundaries of the large austenite grains. Quenching from 1500 degrees Fahr. prevented a resolution

in ferrite which might occur on slow cooling. Only a very small amount of X was available for precipitation in the boundaries of newly formed austenite grains upon reheating. This lowers the coarsening temperature and accounts for the coarse austenite grains found in the samples which were slowly cooled from 2000 to 1500 degrees Fahr., quenched and reheated.

When the samples quenched from 2000 degrees Fahr. were reheated to 1500 degrees Fahr. a large quantity of X was precipitated in the grain boundaries. Quenching retained this dispersion to a large extent. Upon reheating the new austenite grains grew up to but not across the previously precipitated X. For this reason the samples so treated were relatively fine grained but not as fine for B10 as those which were quenched from 2000 degrees Fahr. and reheated directly to the experimental coarsening temperature.

VIII. Conclusions

It is believed that the above experiments prove that aluminum killed steels contain a grain growth inhibitor which has a solubility curve resembling that shown in Fig. 1. Due to this variation of solubility with temperature the grain growth inhibitor may precipitate in the austenite grain boundary and prevent grain growth. Since the solution of grain growth inhibitor in ferrite is an extremely slow process, it is further believed that the fine grains commonly obtained in commercial practice are generally due to previously precipitated X and to the precipitation of X retained in a more soluble form due to rapid cooling rates. Nevertheless, aging steels at 1250 degrees Fahr. may provide a way of raising the grain coarsening temperature.

Although the mechanism offered for inhibited austenite grain growth agrees with the experimental results in a qualitative fashion, quantitative agreement was not obtained. If X is a single chemical substance all aluminum killed steels aged at 1250 degrees Fahr. sufficiently long should have the same quantity in solution and therefore all steels so treated should have the same coarsening temperature. This was not observed. There may, however, be many reasons for this. 1) X may be several substances. 2) Some aluminum killed steels may not have a sufficient quantity of X for saturation at 1250 degrees Fahr. 3) X may distribute itself between the metal and the inclusions just as FeO distributes itself between the slag and the molten steel. In this case the amount of X which may go into solu-

tion depends upon the composition of the inclusions from which it originates.

Solution and diffusion of X at elevated temperatures, where according to the postulate its solubility is relatively high, followed by quenching to retain the X well distributed provides what appears to be an effective means of obtaining fine grains on reheating into the austenite field or in raising the temperature at which grain coarsening will be observed.

This relation should have a valuable application as a pre-treatment for carburizing steels which could be heated to a high temperature and quenched to improve machinability and to prevent undesirable grain growth in carburizing.

IX. Summary

1. A chemical substance (or substances) which is the result of deoxidation with aluminum has, in general, the solubility trend indicated in Fig. 1.

2. The inhibited austenite grain growth of aluminum killed steels is a result of the precipitation of this substance (or these substances) in the grain boundaries of the newly formed austenite grains.

3. Three mechanisms whereby this precipitation may take place are discussed in this paper.

4. The experimental results, in a general way, were found in agreement with these mechanisms.

Acknowledgments

The work herein reported was done under the Research Associate plan of Battelle Memorial Institute and the authors express their appreciation for the opportunity of publishing the results. The authors are especially indebted to Mr. C. E. Sims who took an active part in planning the work and in the preparation of this paper. To Mr. F. W. Boulger, Fellow at Battelle Memorial Institute, they wish to extend their sincere thanks for assistance in some of the early experimental work. Thanks are also extended to Dr. H. W. Gillett for many helpful criticisms and suggestions.

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DISCUSSION

Written Discussion: By J. K. Stone, Research Laboratory, U. S. Steel Corporation, Kearny, New Jersey.

The attempt to give the metallurgist a philosophy on which to base experiments concerning austenite grain size is not new to American Society for Metals gatherings, but this one is a definite step in that direction, and one which should be studied by those of us who are interested in grain growth behavior. It is evident that the authors suspect the rate of heating of samples to be of such importance as to merit inclusion of data concerning the heating rate of the samples they discuss in the text. We have some data which indicate that a slow rate of heating tends to inhibit austenite grain growth. This observation is strictly in accord with the theory and data presented in this paper. The slow rate of heating is qualitatively equivalent to the subcritical treatments used in the authors' work, in that both treatments tend to dissolve the material X and thus have X available for precipitation in the boundaries of the austenite grains formed on heating. The proposed solubility curve of X gives us a plausible explanation for the fairly well known effect of raising the coarsening temperature by a high temperature normalizing operation. I presume the authors would explain this on the basis of their hypothesis somewhat as follows: The high temperature treatment dissolves a large amount of X in austenite and retains it in solution upon cooling, unless the cooling rate is too low; this dissolved X is precipitated in the austenite grain boundaries on subsequent heating and so inhibits grain growth. If this is so, there should be some maximum section size above which the cooling rate in air would not be fast enough to hold X in solution and thus normalizing in that and larger sections would fail to raise the coarsening temperature. If it is true that large sections would cool too slowly to hold X in solution, then we should find normalizing to be less effective in raising the coarsening temperature of large pieces of steel than for small samples of laboratory size. Since large masses of steel must of a necessity be cooled slowly to prevent cracking, it seems logical to point out that, on the basis of the authors' hypothesis, the subcritical solution treatment might be more useful in dissolving X and thus inhibiting austenite grain growth than the method of high temperature normalizing.

The authors' use of the term "aging" for "a long-time treatment" at 800-1000 or 1250 degrees Fahr. is, we feel, misleading. The term "aging" usually implies a precipitation of some constituent, while as far as X is concerned the

treatment is presumed to be one of solution. It is true that carbide is being precipitated but that does not come into the authors' interpretation and furthermore that phenomenon is adequately covered by either of the terms "tempering" or "spheroidizing."

The curve of Fig. 3 showing effect of subcritical solution treatment on subsequent austenite grain size is enlightening but would give us a better picture of grain size behavior if some other value than grains per square inch were plotted. In fact, a number representing grains per square inch is somewhat misleading since it does not cover the case of mixed grain sizes should this condition exist.

The authors, in their conclusion, state that they obtained a qualitative confirmation of the hypothesis by the data, but lament the lack of more consistent quantitative confirmation. Those who have done work along these lines will agree that rigid quantitative relationships are rare, probably because the very basis of grain size work—the rating of grain size—does not lend itself to very precise measurement.

Written Discussion: By R. L. Kenyon and Harry Tobin, American Rolling Mill Co., Middletown, Ohio.

In discussing the effect of holding steel just below the A_3 point ("aging treatment"), the authors have not mentioned the well known effect of such a treatment on the spheroidization of the carbides. The authors found that "aging" for a considerable time was necessary to cause any inhibiting effect on grain growth, and have interpreted this in terms of the effect on a grain inhibiting a component which they call X, but which they infer is probably alumina. Is it not possible that the long aging treatments resulted in the formation of large spheroids of carbides which did not go into solution in the relatively short time of one hour for which the authors heated the specimens subsequent to the aging treatment? No doubt these carbides would serve as grain growth inhibitors.

The authors report that their "aging" treatment was effective only when applied for longer periods of time, and at temperatures which are most favorable for carbide spheroidization. We should like to ask if the authors have investigated the effect of heating the specimens at the higher final temperature of 1650 or 1750 degrees Fahr. for periods longer than one hour, because they state at the conclusion of the paper that the pretreatments used would be effective in preventing undesirable grain growth during carburizing, and yet such work ordinarily requires much longer than one hour at the higher temperatures.

Written Discussion: By Alan U. Seybolt, assistant metallurgist, Battelle Memorial Institute, Columbus, Ohio.

During the course of some work performed at Hammond Laboratory on the solid solubility of oxygen in the metals of the iron group, the solid solubility of oxygen in iron was determined, the results of which will be published in the near future.

The shape of the solubility curve found is identical in form with the solubility curve of "X" in aluminum killed steels as qualitatively established by Dorn and Harder.

As the temperature of alpha iron is increased toward the alpha to gamma transformation, the solubility of oxygen increases rapidly with temperature, but

when the iron undergoes the transformation, the oxygen solubility is at once diminished to about one-quarter of the solubility just below the transformation temperature. As the temperature of gamma iron is raised, the solid solubility of oxygen again increases with temperature. The solid solubility of oxygen in commercial aluminum killed steels obviously must be far different from the solubility in high purity iron. Nevertheless, it is safe to assume that there is some oxygen solid solubility in such steels and that the solid solubility curve of temperature versus oxygen concentration should take the same form as the curve for iron.

If, as seems reasonable, the grain inhibiting substance is a substance containing oxygen, and if this inhibitor may be formed by the process of oxygen diffusion in the steel, the results outlined above may help to rationalize the experimental data found for the aluminum killed steels.

When the steels were furnace cooled from 2300 degrees Fahr., most of the inhibiting material should have precipitated, as the authors have pointed out. If the amount of inhibiting material which had precipitated at the end of this treatment was less than the solid solubility limit at 1250 degrees Fahr., and assuming that more inhibiting material can form by oxygen diffusion at 1250 degrees Fahr., the effectiveness of such a solution treatment is readily explained. The inhibitor being more soluble in ferrite than in newly formed austenite, and being present in greater quantity after the aging treatment, precipitates in the austenite on reheating and effectively reduces grain growth. The oxygen atoms which are able to diffuse and enter into combination to form the inhibitive material may originate from two sources; first, diffusion from the surface scale and second, diffusion from inclusions.

Written Discussion: By E. H. Dix, Jr., Research Laboratories, Aluminum Co. of America, New Kensington, Pa.

This paper presents a valuable compilation of experimental results and an interesting hypothesis which seems to satisfactorily explain the observed facts. The hypothesis would be considerably strengthened if it could be shown that no other of the commonly accepted mechanisms can be used to equally well explain the experimental observations.

The paper gives the steel man a rather simple and very logical explanation for that which must have troubled him for years, namely, how do pretreatments affect the grain coarsening characteristics obtained on reheating. Unfortunately the steel man is not the only one who is troubled in attempting to obtain an explanation, for often unexplained behaviors of metals possessing only one crystal form occur during simple recrystallization after cold work.

In the case of the metal aluminum and its alloys the effect of grain growth inhibitors or substances which affect and control the grain size seems to be most satisfactorily explained on the basis of what might be termed the "necular theory", rather than the theory of the "interference envelope" which has been accepted and used by the authors in developing their hypothesis.

My purpose in discussing this paper is a selfish one, namely, to try to determine whether the experimental evidence presented by the authors can be used to throw additional light on the relative possible truthfulness of the two mechanisms for inhibiting grain growth previously mentioned. I have read and studied the paper with this idea in mind. My conclusions are only partially

satisfactory and I am focusing attention on this phase of the authors' paper in the hope that they or persons present at this meeting will arrive at more satisfactory conclusions than I have been able to.

Time is not available to consider in any detail the mechanism of recrystallization itself. This might well be a subject for one entire session. However, when we consider specifically the action of grain growth inhibitors we might well start with the simplest case, namely, that of solidification from the liquid state. I believe that there is fairly general agreement that particles of high melting point floating around in a liquid metal may act as nuclei or seeds in initiating crystal centers. Of course, the greater number of crystal centers formed, the sooner adjacent grains will touch and interfere with further grain growth.

A similar mechanism might be postulated for recrystallization after cold work, although here we run into the difficulty that there seems to be no general agreement as to the mechanism of recrystallization. In the case of the steels with which the authors have worked the situation is again different because they are dealing with a phase change and a complete rearrangement of the crystal structure.

Let us turn to the conclusions to which the authors are led on the basis of the tests described up to page 113. Conclusions 1 and 2 are quite in accord with the types of solubility curves which the authors have postulated. Conclusion 3 which reads, "the excess X in solution in ferrite over the saturation value in austenite precipitates in the grain boundaries of the newly formed austenite grains and prevents grain growth." May not I equally well say that the material X which has been in solution in the ferrite is precipitated in a fine state of dispersion at the instant of the change from the ferrite to the austenite and that these tiny particles seed the formation of the newly formed austenite grains. Of course, I would also have to say that the portion of the material X precipitated by aging treatments in the ferrite had grown to a particle size which was beyond that effective in acting as nuclei.

When we turn, however, to page 124, in which the authors postulate that in samples quenched from 2000 degrees Fahr. and reheated to 1500 degrees Fahr. a large quantity of X was precipitated in the grain boundaries and largely retained there by quenching. Then upon reheating the new austenite grains grew up but did not cross the previously precipitated cellular X material. I have tried to explain the results of these latter experiments on the basis of the nuclear theory and I can do it to my satisfaction to the extent of the control of the initial grain size which may be obtained by reheating to the temperatures specified but I cannot quite so satisfactorily explain the definite and apparently more or less critical "coarsening temperature." I am not sure, however, that this cannot be explained on some other basis than that of the behavior of material X. Maybe the authors with their more intimate knowledge of the detailed conditions of their experiments or someone in the audience may be able to help me in that connection.

Aside from the factors mentioned I think it is a matter of some very considerable fundamental importance to determine just how foreign particles behave during solidification, recrystallization and phase changes. The direct evidence which we can obtain in the case of aluminum by microscopic examina-

tion is of no help because the particles which we are interested in must be of a submicroscopic size. It is a matter of common knowledge that during solidification low melting point eutectics are rejected to the grain boundaries and interstices of the dendrites. The generally discontinuous envelopes of coarse constituent visible under the microscope evidently have no effect in controlling grain size. When such a cast structure is severely worked these particles are lined in the direction of rolling but again, because of their large size, have no influence whatsoever on the recrystallized grain pattern, so this sort of visual evidence is of no help.

Tammann, many years ago, performed an experiment with the metal cadmium. By dissolving the metal with a suitable technique he found a residual cellular film which he felt was related to the grain size of the metal and that it was this film which had controlled the grain size. More recently, Dr. H. F. Freche, working in our laboratories, attempted to duplicate the experiment and found a cellular film structure but in this case it certainly was not anything of the same order of magnitude as the grain size.

Having talked for some considerable period, I can probably sum up my remarks by expressing considerable difficulty in accepting the postulation that material of relatively low solubility can be rejected to the grain boundaries during the simple recrystallization of cold work, single phase, metals and it seems to me that this same objection applies in the case of new crystals formed subsequent to a phase change.

Oral Discussion

HARRY P. COATES:[1] It seems to me that there are possibilities of measuring this "X", this unknown quantity, by some additional methods. If we want to hold the samples at 1250 degrees Fahr. and dissolve "X" we may then cool quickly and age at say 500 degrees Fahr., and then we may measure the yield point, or the tensile strength, or the Rockwell B hardness. Now according to this curve it seems that we might also heat over the austenitic boundary, and then cool rapidly, such as air cooling, and then measure those same properties. That is, we may have two ways of measuring age hardening after dissolving the constituent "X", which may cause the age hardening. This was no part of the paper, but the question I wish to ask is this:

Have those properties, such as hardness and tensile strength and yield point, been measured at those different temperatures?

Authors' Reply

The authors are pleased with the discussion this paper has stimulated. The mechanism offered for the relation of pretreatment of steels to the austenitic grain growth characteristics was presented with one of the purposes being to stimulate discussion and another to have the proposed hypothesis given the acid test in other research laboratories. If further work proves that this mechanism is untenable the authors will be glad to welcome a better mechanism. For the present, however, more extensive tests both in the laboratory and in practice seem desirable.

[1]Chief chemist, Firestone Steel Products Co., Akron, Ohio.

Mr. Dix has raised some very good points in connection with the proposed mechanism. It is known that foreign bodies such as refractory substances can function as nuclei for the solidification of metals and alloys and for the precipitation of phases on cooling as, for example, the separation of hypoeutectoid ferrite from a supersaturated solution of austenite. This phenomenon is also known in "seeding out" of supersaturated aqueous solutions. It is difficult to conceive of a foreign substance, alumina, for example, functioning to cause nucleation in the formation of austenite on heating because austenite nucleation is a solution reaction between ferrite and cementite at the interfaces of these two phases. So far as the authors are aware no experimental evidence has ever been presented to show that small grains of austenite form around a nucleus of a foreign body. On the other hand, the austenite grains on forming as nuclei tend to reject impurities.

This mechanism may not have a true counterpart in aluminum alloys and apparently does not have in the case of cold-worked aluminum of high purity. Possibly in some of the alloys a similar mechanism may exist. Thus, in the authors' opinion the nucleation theory does not seem applicable to the control of the austenite grain size and the film theory or the rejection of the impurities to the austenite grain boundaries is favored.

The authors invented the hypothetical substance "X" in order to avoid reference to alumina as the active agent for inhibiting austenite grain growth because it was realized that compounds of metals other than aluminum and compounds of aluminum other than the oxide might be effective in this mechanism.

In reply to Messrs. Kenyon and Tobin's discussion of the effect of carbides, the differences in grain growth reported were observed in some cases in which the specimens had been given relatively long subcritical solution treatments which were favorable to spheroidization of the cementite. Microscopic examination of specimens after these subcritical treatments did not show differences in the size of the carbide particles. Further, in no case in which the grain growth tests were made was any undissolved carbides noted after the grain coarsening treatment. It is more likely that coarse spheroidized carbide particles will play an important part in preventing grain growth of eutectoid and hypereutectoid steels than in the hypoeutectoid steels studied in this investigation.

The point raised by Messrs. Kenyon and Tobin was considered and some of the experiments were directed to a study of this relation. Duplicate samples were treated as shown in Table I and investigated immediately after operation V. All steels for both types of heat treatment showed the same degree and type of spheroidization when examined microscopically. No residual cementite was found after holding the spheroidized specimens three-quarters of an hour at 1550 degrees Fahr. Furthermore, the results obtained in Section VI apparently cannot be attributed to spheroidization.

While it is likely that there will be some difference in the austenite grain size initially developed when formed from specimens containing mostly lamellar pearlite as compared with those containing spheroidized cementite, it is not considered that that difference was involved in this investigation and differences due to the size of cementite particles are thought to be of minor importance.

The authors appreciate Dr. Seybolt's interesting addition to their paper.

Certainly, if both oxygen and aluminum have lesser solubilities in the lower temperature regions of austenite than in the higher temperature regions of ferrite, the solubility product for aluminum, $K = (Al)^2 \times (O)^3$ should show the same trend. As Dr. Seybolt carefully points out, however, this offers a plausible explanation but is not necessarily proof that alumina is the active agent.

Mr. Stone's contribution to the discussion of this paper is most welcome. Apparently the effect of the rate of heating and the normalizing temperature upon the future austenite grain size can be accounted for by the hypothesis presented in this paper. The selection of the term "aging" for the long-time subcritical treatment may not be the best in view of its specialized meaning in the process of precipitation hardening. Possibly the term "solution aging" could be used unambiguously in this case.

Mr. Stone has raised an important point with reference to the application of rapid cooling from a high temperature solution treatment to the raising of the coarsening temperature of the austenite grains on reheating. Experiments so far indicate that the more rapid rate of cooling is more effective. Presumably, some beneficial effects may be obtained in large sections with permissible cooling rates. The subcritical solution treatment may be found impractical because of the relatively long time required for solution and diffusion. Further information is needed on this phase of the application.

Mr. Coates has suggested measuring some of the physical properties of pretreated steels in order to test the validity of the grain boundary precipitation hypothesis. The authors believe that it would be very difficult to change the condition of X in the steel without simultaneously producing other changes. For this reason, no such attempt was made.

In conclusion, the authors look forward with much interest to further reports on the application of the proposed hypothesis and it is hoped adverse as well as favorable results will be reported.

AUSTENITIC GRAIN SIZE OF EUTECTOID STEEL

By Harry Tobin and Reid L. Kenyon

Abstract

It is difficult to determine the austenitic grain size of eutectoid steel by ordinary methods of examination due to the difficulty in distinguishing between the different grains. The paper presents a special technique by which the size of the austenitic grains in this range of steels can be very clearly shown, and also gives a modification which makes it possible to determine the size of the prior austenitic grains on a piece of material which has already been heat treated. This method of examination has been applied to a study of the effect of previous austenitic grain size and rate of heating through the critical temperature on the resultant austenitic grain size. An investigation has also been made using this technique to show the characteristic austenitic grain growth behavior of a eutectoid steel. It is brought out in the paper that only by such a study can the behavior of a steel be determined for the entire range of heat treatments to which it may be subjected.

Introduction

THE effect of the size of the austenitic grain on the properties of steel has received a great deal of attention in the last few years. Most of the published work on this subject has appeared since 1934, the year of the A.S.M. Grain Size Symposium, and has dealt largely with the effect of austenitic grain size upon the properties of the steels rather than the factors which affect the austenitic grain size itself.

The objects of this paper are: to present a method of determining the austenitic grain size of eutectoid steel, and by use of this method to show the effect of certain factors on the austenitic grain size of such material. The work was all carried out on one lot of basic open hearth hot rolled strip of the following composition:

	Per Cent
Carbon	0.80
Manganese	0.74
Silicon	0.21

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. Of the authors, Harry Tobin is Research Assistant, Research Laboratories, and Reid L. Kenyon is Research Metallurgist, Research Laboratories, The American Rolling Mill Company, Middletown, Ohio. Manuscript received June 25, 1937.

Method of Determining Austenitic Grain Size

In order to reveal the austenitic grain boundaries in eutectoid steels, one of three general methods may be used. First, the grain boundaries can be outlined by structural components, such as pro-eutectoid cementite or ferrite resulting from differences in composition produced either by carburization[1] or decarburization;[2] second, differences in structure, such as the presence of pearlite at the grain boundaries, can be developed[3] by suitable heat treatment and etching; or third, the grain boundaries themselves can be developed by suitable chemical reagents which have a differential attack on the grain boundary material.[4] Suitable etching of martensitic structures will develop the different orientations in the grains, and thus give an idea of the grain size, though the boundaries are not distinct.

These various methods have been discussed elsewhere,[5] and it is unnecessary to describe them here. The method which we have found best for eutectoid steels is a combination of the first and third general methods mentioned above.

In the first place, it must be emphasized that the grain boundaries that are to be revealed are the ones which were present at the high temperature at which the austenite occurs. By providing for a suitable amount of surface oxidation at high temperature, the boundaries of the austenitic grains will be attacked. This alone will outline the austenitic grain boundaries faintly, but we have found that it is better to supplement this by a suitable etching treatment. This results in the development of a network of grain boundaries on the specimens (as shown in the photomicrographs) which are the boundaries of the prior austenite grains.

The specimen is ground smooth and polished as for metallographic examination, except that the final operations on the wet wheels are omitted. It is then heated in a mildly oxidizing atmosphere under the particular time and temperature conditions that are to be studied. When the temperature is not too high, and the time not too long, ordinary furnace atmospheres are quite satisfactory.

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[1]McQuaid-Ehn test falls under this classification.

[2]Described by P. Herasymenko, *Metal Progress*, September 1936, p. 69.

[3]Differential quenching method described by Davenport and Bain, TRANSACTIONS, American Society for Metals, Vol. 22, 1934, p. 879.

[4]Described by J. R. Vilella and E. C. Bain, *Metal Progress*, September 1936, p. 39.

[5]A.S.M. Metals Handbook, 1936 Edition, p. 584.

At 1700 degrees Fahr. (925 degrees Cent.) and higher temperatures, it may be necessary to limit the surface oxidation by packing the sample in some material that limits the access of the furnace atmosphere. The sample can be packed in powdered charcoal, red iron oxide, or iron filings. On the other hand, it can be heated in a suitable salt bath, or enclosed in a small container, provided it is exposed to oxidizing conditions for a few minutes at the end of the soaking period.

Following the heat treatment just described, the specimen may be cooled either slowly or by quenching.[6] If slowly cooled, the oxidized boundaries of the austenite grains will show as white ferrite films in the specimen after repolishing and etching, while if drastically quenched, the subsequent etching of the repolished sample brings out a black grain boundary network on a white field which looks very much like the structure of pure iron. In some cases the detail of the martensitic structure of the grains is also visible, but is not sufficiently prominent to mask the black outlines of the boundaries.

Inasmuch as the prior austenitic grain boundaries can be brought out by this method, even after slow cooling, it is possible to determine the austenitic grain size developed by a previous heat treatment, even though the sample was not especially prepared by grinding and polishing previous to this heat treatment. After the sample has been heat treated and cooled either slowly or by quenching, the surface is carefully polished, first on the finer grades of Huber paper, and then with the regular wet wheels used for metallographic polishing. Too much metal should not be ground away; otherwise, all of this surface layer on which the grain boundaries have been attacked will be removed. Sometimes the surface has been severely pitted during the heat treatment, and it may be impossible to remove all these pits in the final polishing operation.

The etching treatments used depend somewhat on the method of cooling. If the sample has been slowly cooled, the usual reagents for eutectoid steels may be used such as picral or nital. The samples which have been quenched and have a martensitic structure are best etched with a 15 per cent solution of HCl in ethyl alcohol. The sample is placed in a dish of the solution with the polished surface up. When the surface becomes dull or grey, it

[6] In this respect it differs essentially from the method of Davenport, Bain, and from that of Herasymenko.

is sufficiently etched. This may require from one to ten minutes. This solution can also be used on the pearlitic structures, but does not bring out the details of the pearlite as well as picral or nital.

A piece of eutectoid steel was heated six hours at 2000 degrees Fahr. (1095 degrees Cent.) in a closed container, having a limited amount of air, and then slowly cooled. After polishing and etching

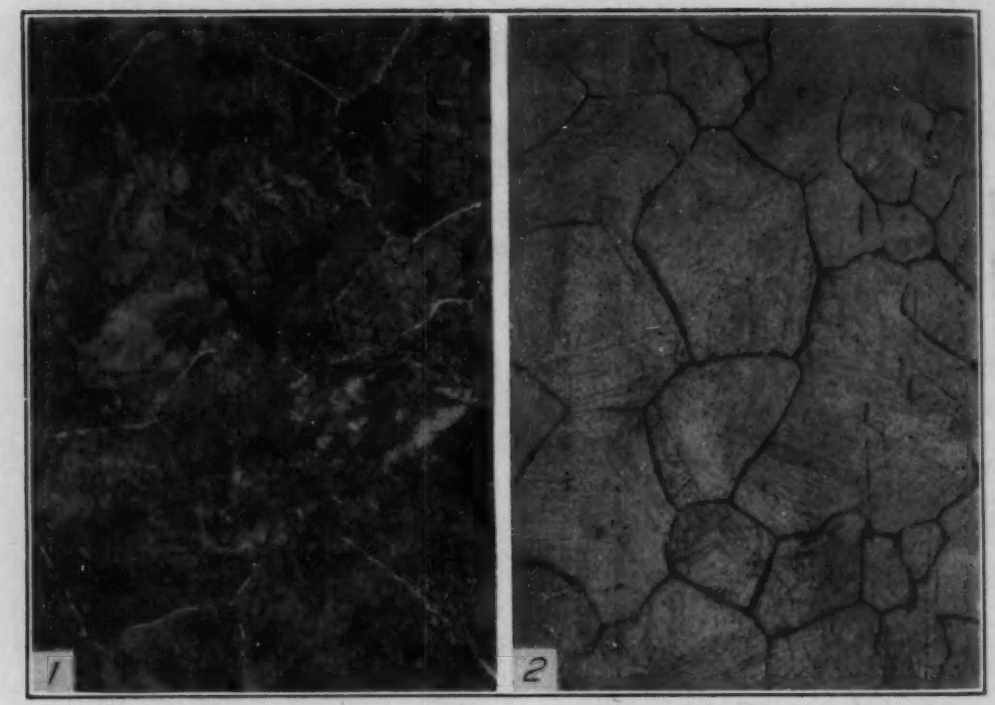

Fig. 1—M-18702. Specimen of Eutectoid Steel Heated 6 Hours at 2000 Degrees Fahr. in Closed Container with Limited Amount of Air. Slowly Cooled. Etched with Nital. × 100.

Fig. 2—M-18191. Specimen from Same Piece of Eutectoid Steel as Shown in Fig. 1, Heated 6 Hours at 2000 Degrees Fahr. in Closed Container with Limited Amount of Air. Quenched in 10 Per Cent Brine Solution. Etched with 15 Per Cent HCl in Ethyl Alcohol. × 100.

by the above method, the sample showed the structure of Fig. 1. The grain boundaries are identified by the ferrite envelopes. Another piece of the same steel was heated for the same length of time, at the same temperature, then quenched in a 10 per cent brine solution. The sample was protected from excessive oxidation during the heating as before. The grain boundaries in this case, as shown in Fig. 2, are dark due to the greater solubility of the grain boundary material in the alcoholic hydrochloric acid etching solution. Some detail can also be observed in the martensitic structure within the grains.

The application of this method to a piece of steel which has already been heat treated is shown in Fig. 3. This is a specimen cut from a forging. It was carefully polished on one of the original outside surfaces. The oxidation of this surface during its regular heat treatment had penetrated along grain boundaries, so that by careful polishing the prior austenite grains are seen to be outlined by a white network of ferrite. Another piece of this steel was ground and polished according to the method described above, and reheated under the same conditions as the specimen shown in Fig. 3 (2 hours at 1500 degrees Fahr.). This sample was quenched in brine and etched in 15 per cent alcoholic hydrochloric acid, with the result shown in Fig. 4. It will be seen that under both conditions, the austenitic grain size is the same, thus showing the accuracy of this method in determining the previous austenitic grain size on a specimen which has been heat treated in some commercial process.

The reliability of the method has been further checked by comparing the grain size at the surface as developed by the above procedure, with that in the interior of the piece as shown by other methods such as the outlining of the grains with a pearlite network. A specimen was given a differential quench according to the method described by Vilella and Bain.[7] The structure at the surface of the severely quenched portion of the specimen is shown in Fig. 5, while Fig. 6 shows the structure at the surface in the intermediate zone where the grains are outlined by pearlite. Attention is called to the fact that the sharp outlines of the grain boundaries in Fig. 5 reveal the presence of numerous small grains that are obscured by some of the larger patches of pearlite in Fig. 6, and, therefore, cannot be shown by that method. The specimen was deeply ground below the surface in the region of the spot shown in Fig. 6, and again polished and etched. It then revealed the structure shown in Fig. 7. Inasmuch as the entire specimen was subject to the same degree of mild oxidation during the heat treatment, it is believed that this comparison of the austenitic grain size in different portions of the same piece at the surface, with that at the mid-thickness, proves the reliability of this method.[8] It may also be mentioned that the austenitic grain size is the same in those portions of the specimen which were

[7] *Metal Progress*, September 1936, p. 39.

[8] This procedure for verifying the method on aluminum treated or other steels having a slow rate of grain growth is not applicable, due to the rapid rates of transformation of such steels to pearlitic structures. The only confirmation on such material is that the grain size determined by the proposed method is of the same order as that reported by other investigators.

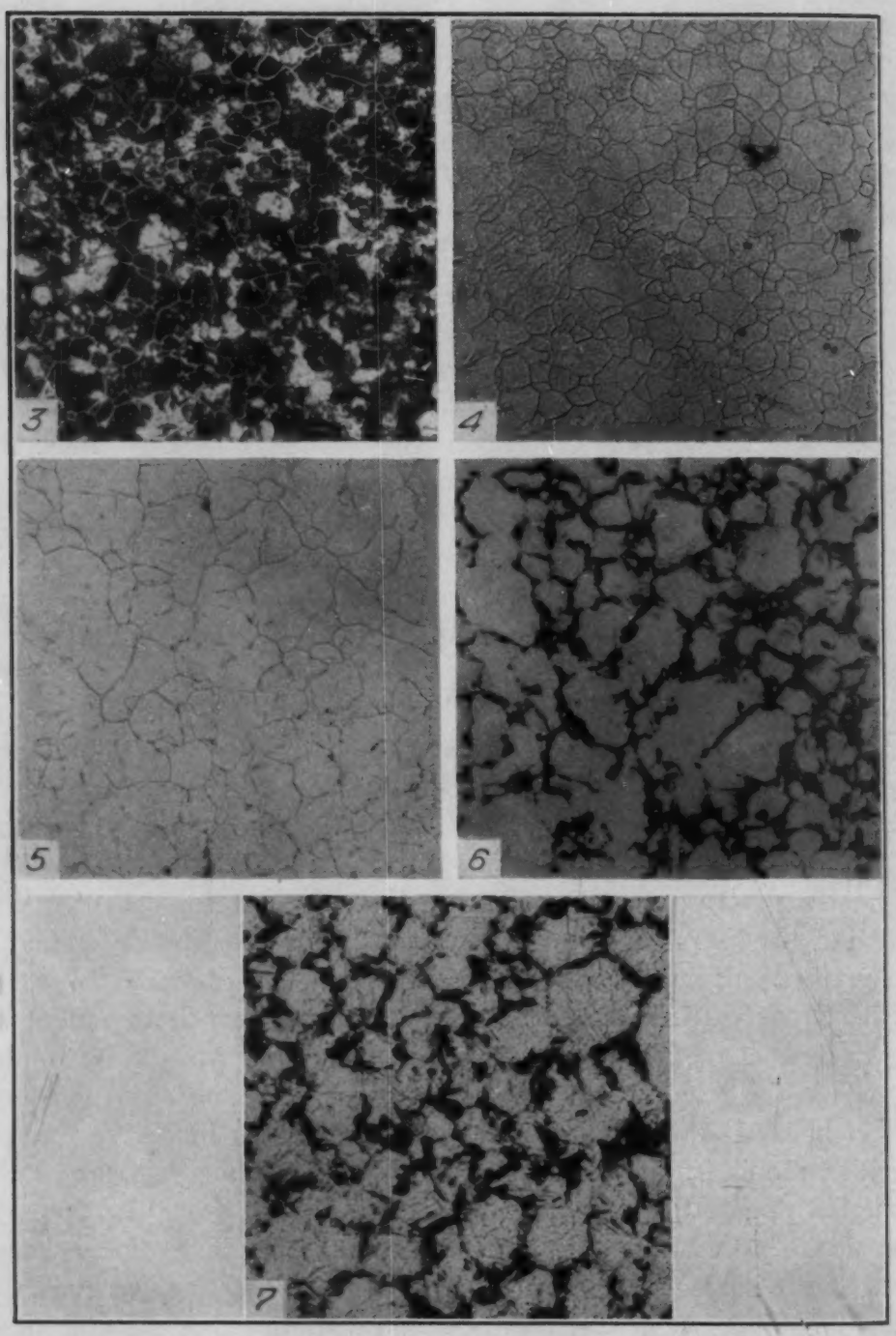

Fig. 3—M-18879. Specimen from Large Forging of Eutectoid Steel. Original Surface Polished. Etched with Nital. × 100.

Fig. 4—M-18954. Specimen from Same Forging as Shown in Fig. 3. Surface Prepared as Described in Text, Reheated 2 Hours at 1500 Degrees Fahr. (Same Heat Treatment as Used for Original Forging), Quenched in Brine, Repolished, Etched with 15 Per Cent HCl in Ethyl Alcohol. × 100.

Fig. 5—Differentially Quenched Specimen of Eutectoid Steel Showing Austenitic Grain Size at Surface of Quenched Portion. Etched with 15 Per Cent HCl in Ethyl Alcohol. × 100.

Fig. 6—Same Specimen as Fig. 5 Showing Austenitic Grain Size at Surface of Intermediate Zone. Etched with Nital. × 100.

Fig. 7—Same Specimen as Figs. 5 and 6 Showing Austenitic Grain Size Beneath the Surface Under Spot Shown in Fig. 6. Etched with Nital. × 100.

cooled rapidly enough to form martensite as in those which were cooled slowly enough to develop pearlite in the grain boundaries and even to be completely pearlitic.

Effect of Previous Austenitic Grain Size

On account of the wide interest as to the effect of previous austenitic grain size on the grain size developed in subsequent heat treating operations, one of the first applications which the authors made of the above method of developing the austenitic grain size was to study this effect in an eutectoid steel. Two pieces of the same hot-rolled steel which was described previously were heat treated so as to make one fine-grained and the other coarse-grained. To do this, one was heated 30 minutes at 1500 degrees Fahr. (815 degrees Cent.) and air-cooled, which produced a No. 6 grain size, while the other piece was air cooled after soaking six hours at 2000 degrees Fahr. (1095 degrees Cent.), which produced a No. 2 grain size. Portions of these two pieces were then heated four hours at 1400, and two hours at 1500, 1600, 1700, and 1800 degrees Fahr. (815, 870, 925 and 980 degrees Cent.). Examination of these specimens showed the final grain size to be the same on corresponding specimens regardless of whether they came from the coarse or the fine grained piece.

A group of four photomicrographs is shown in Fig. 8, representing the coarse- and fine-grained structures developed in the two original pieces, and the fine grains in the same pieces after subsequent heating four hours at 1400 degrees Fahr. (760 degrees Cent.). It will be seen that the resultant austenitic grain size is uninfluenced by the previous austenitic grain size.

Effect of Rate of Heating Through the Critical Temperature

A further application of this method was made in studying the effect of heating rate on austenitic grain size. Specimens about 0.050-inch thick were heated at rates of 1 degree, 12 degrees, and 800 degrees Fahr. per minute through the interval of 1300 to 1400 degrees Fahr., which included the critical temperature. They were then held at 1400 degrees Fahr. (760 degrees Cent.) for one hour, quenched in brine and examined according to the method previously

described. All specimens had a No. 6 grain size. This same procedure was repeated on another series of specimens, except that they were heated to 1500 degrees Fahr. (815 degrees Cent.) and held for one hour. The samples which were heated at the three different rates again had the same grain size, which in this case was No. 5½. Thus, the austenitic grain size of this steel was independent of the investigated rates of heating through the critical.

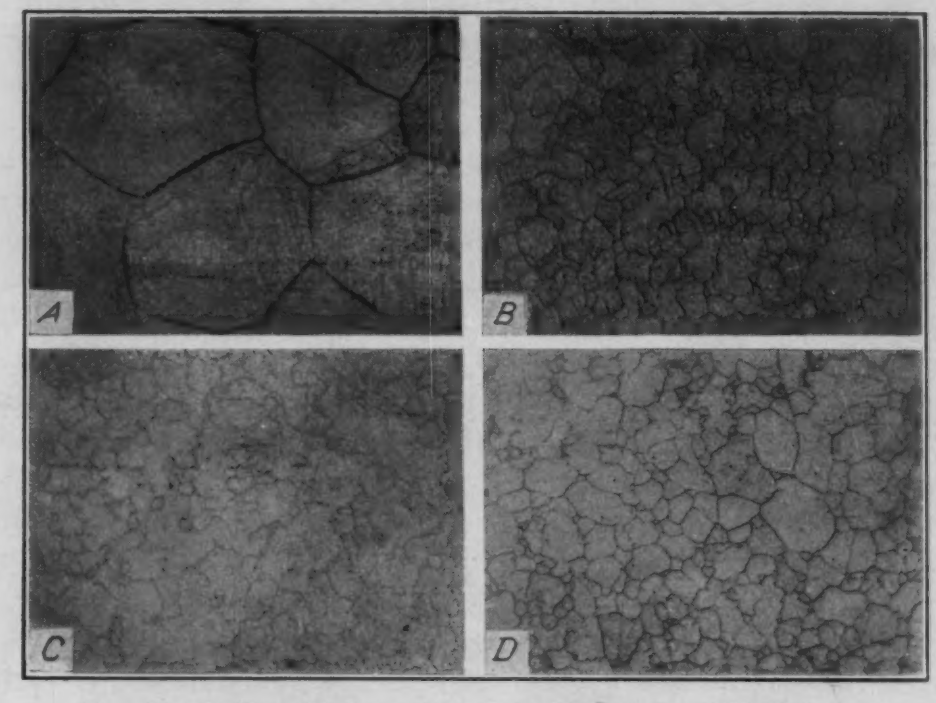

Fig. 8—Four Specimens from Same Piece of Eutectoid Steel.
(a) Heated 6 Hours at 2000 Degrees Fahr. Which Produced Coarse Austenitic Grains.
(b) Heated 30 Minutes at 1500 Degrees Fahr. Which Produced Fine Austenitic Grains.
(c) Same as (a) After Reheating 4 Hours at 1400 Degrees Fahr.
(d) Same as (b) After Reheating 4 Hours at 1400 Degrees Fahr.
All Specimens Quenched in Brine After Final Heat Treatment and Etched with 15 Per Cent HCl in Ethyl Alcohol. × 100.

Effect of Time and Temperature

A common method of studying the austenitic grain size of steel is to heat treat it at some arbitrarily chosen temperature for a definite length of time. An example is the McQuaid-Ehn test, in which the specimen is heated in a carburizing compound usually for eight hours at 1700 degrees Fahr. (925 degrees Cent.). Another method is to heat the specimen in a furnace under definite time and temperature conditions, and then quench it and examine a fractured surface. The austenitic grain size determined by these methods gives

what has been termed the "inherent grain size" of the steel. This test under one set of time and temperature conditions has been assumed by some to indicate the behavior of the steel under other widely different heat treatments. However, this complete behavior can only be determined by subjecting the steel to each particular condition under consideration. In other words, the McQuaid-Ehn test or any other test applied to only one combination of time and temperature represents only one point in an entire two dimensional co-ordinate system, and the behavior of a particular steel under widely different conditions cannot be accurately judged from the results of a single test.

The steel used in this investigation has been subjected to a variety of heat treatments covering the ranges of time and temperature that would be employed in the usual heating, working, and heat treating operations on this material. While it should possibly be extended to higher temperatures in order to represent some of the working operations in the initial reductions from the ingot, the finishing temperatures are usually within the ranges investigated and all annealing and quenching operations would be well within the range which has been studied.

Specimens of hot-rolled strip about 0.050 inch thick were heat treated according to the described method for various lengths of time at various temperatures as indicated in Table I. These speci-

Table I

Austenitic Grain Size (A.S.T.M. Standard Nos.) After Various Heat Treatments

Temp. Degrees Fahr.	Time at Temperature in Minutes										
	1	3	10	30	90	240	900	1500	3000	4500	5520
1400	...	...	...	7	...	6	6	5½	5	5	5
1500	...	...	7	6½	6	6	4½	...	...	...	...
1600	...	...	6½	5	5	4½	3	...	...	...	...
1700	...	6½	5½	5	4½	4	3	...	...	...	...
1800	...	5	4	4	3	2	...	...	...	...	...
1900	5½	4½	4	3½	3	2	...	...	...	...	...

mens were all quenched in brine and etched in alcoholic hydrochloric acid. They were then photographed at 100 diameters for grain size estimation. On account of the large number of micrographs involved, and duplication of structures found on different specimens, only a few representative ones will be shown.

In comparing the various photomicrographs with the A.S.T.M. grain size charts, a number of instances were encountered in which it was difficult to decide whether the grain size was, say, 5 or 6. The

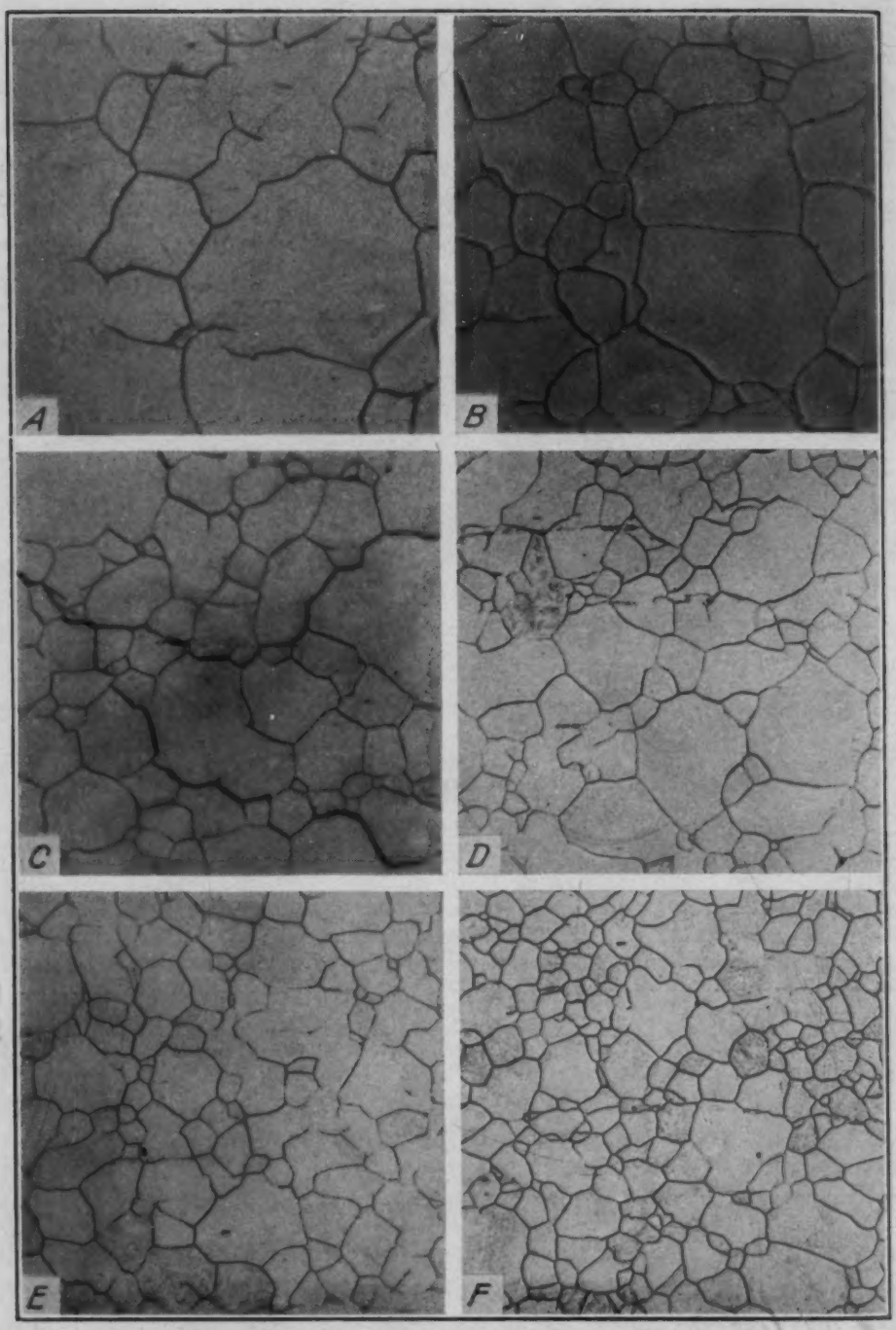

Fig. 9—Typical Austenitic Grain Sizes Developed in Eutectoid Steel by Heating at Different Temperatures for Various Lengths of Time as Shown in Fig. 10.

a—American Society for Testing Materials Grain Size 2
b—American Society for Testing Materials Grain Size 3
c—American Society for Testing Materials Grain Size 3½ (note crack through austenitic grain boundaries)
d—American Society for Testing Materials Grain Size 4
e—American Society for Testing Materials Grain Size 4½
f—American Society for Testing Materials Grain Size 5

simple black line network of grain boundaries in these micrographs made it easier to get an impression of the grain size by visual examination than in the microstructures usually developed in eutectoid steels, and, therefore some of these structures have been graded to half a grain size number. In doing this, an effort was made to

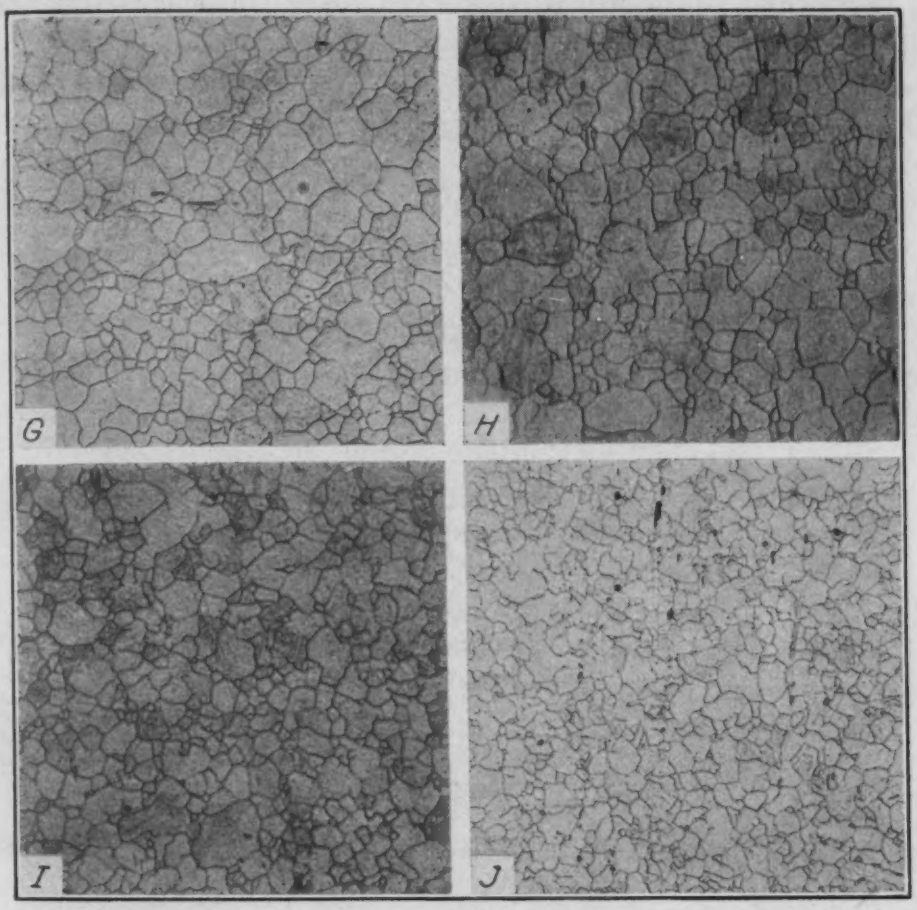

Fig. 9—(Continued) Typical Austenitic Grain Sizes Developed in Eutectoid Steel by Heating at Different Temperatures for Various Lengths of Time as Shown in Fig. 10.
g—American Society for Testing Materials Grain Size 5½
h—American Society for Testing Materials Grain Size 6
i—American Society for Testing Materials Grain Size 6½
j—American Society for Testing Materials Grain Size 7

average the larger grains against the smaller ones, and strike an average to compare with the standard grain size charts. Table I gives the results of these grain size estimations on all of the specimens, and Fig. 9 shows a typical specimen of each of the different grain sizes encountered.

The data in Table I show a progressive increase in grain size with time at all of the temperatures investigated. In order to indi-

cate this more clearly, the data have been plotted in Fig. 10 with time on a logarithmic scale. While there is some variation in the position of the points for a given temperature, the tendency seems to be for them to lie on straight lines. This means that the curve relating austenite grain size with time at a given temperature is of an exponential form which is believed to be consistent with other published data on grain growth.

The one important conclusion that can be drawn from this

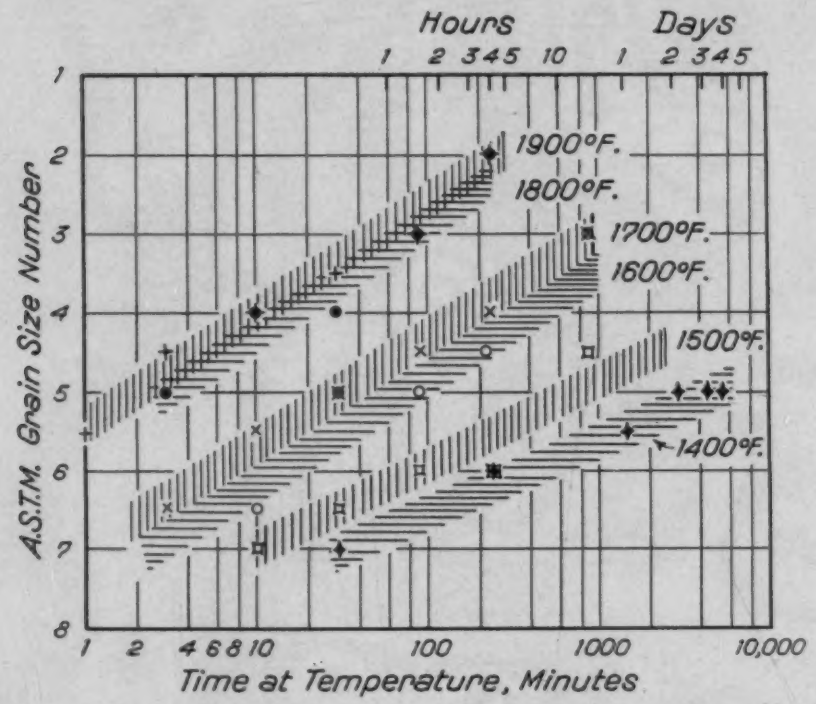

Fig. 10—Effect of Time and Temperature of Heating on the Austenitic Grain Size of an Eutectoid Steel.

investigation is that the austenitic grain size is a function of the time and temperature to which the steel has been subjected, and cannot be predicted from tests that have been made on the steel when subjected to only one condition of time and temperature. A steel does not have an inherent grain size in the sense that it will always be coarse- or fine-grained under all conditions of heat treatment. The grain will be fine or coarse, depending on the time and temperature of heating. Instead of having an inherent grain size, it is believed that a steel has a *characteristic austenitic grain growth behavior* which is dependent on the time and temperature factors.

In order to understand this austenitic grain growth behavior of a particular steel it is necessary to study it under various condi-

tions, as in the example given. Inasmuch as the austenitic grain growth behavior may differ with composition and from heat to heat of the same nominal composition, it will probably be necessary to conduct this type of investigation on each lot of material in order to determine its behavior under the various conditions of heat treatment.

If the steel is to be heat treated under only one set of time-temperature conditions, it may be sufficient to study the grain growth behavior under these conditions alone. However, if the steel may be used for a wide variety of purposes under widely different heat treatments, nothing short of a diagram similar to Fig. 10 will serve as an adequate guide to the grain growth behavior of the material. By the use of such a chart, the time of heating at various temperatures could be controlled in order to obtain the desired grain size. For example, a steel which showed a fine grain after heating, say, eight hours at 1700 degrees Fahr. (925 degrees Cent.), would be expected to be fine-grained after heating at lower temperatures or for lengths of time less than eight hours. On the other hand, a steel which was coarse-grained after heating eight hours at 1700 degrees Fahr. (925 degrees Cent.) might be heat treated at some lower temperature or shorter time so as to produce a satisfactorily fine grain.

When microscopic equipment is not available, or where it is more convenient to make fracture tests on quenched specimens, that method of investigating grain size can be used due to the close relationship between the fracture test and the austenitic grain size. This is due to the fact that the fractures of martensitic steels occur along the grain boundaries. This is shown in Fig. 9c, where the quenching cracks very definitely follow the grain boundaries. The important point to be observed in using the fracture test is the same as in the case of microscopic examination: the entire range of time and temperature must be investigated in order to determine the characteristic austenitic grain growth behavior.

Summary and Conclusions

1. The austenitic grain size of eutectoid steel can be determined by heating the specimen under mildly oxidizing conditions followed by careful polishing and etching in a 15 per cent solution of hydrochloric acid in ethyl alcohol.

2. The previous austenitic grain size can be determined on one

of the original surfaces of a heat treated piece, provided it has been subjected to oxidation, decarburization, or the corrosive attack of a salt bath. Light polishing of the surface is followed by etching with sodium picrate or nital with slowly cooled samples, or with alcoholic HCl in the case of martensitic specimens.

3. On the eutectoid steel investigated, the austenitic grain size developed by a particular heat treatment was not influenced by the austenitic grain size resulting from previous treatments.

4. The rate of heating through the critical temperature, within the limits of 1 to 800 degrees Fahr. per minute, did not affect the austenitic grain size on the eutectoid steel used in these tests.

5. Instead of having an inherent grain size, it is believed that a steel has a *characteristic austenitic grain growth behavior* which is dependent for that steel on the time and temperature factors. Variations in composition will undoubtedly affect this grain growth behavior.

ACKNOWLEDGMENT

The authors express their appreciation of the encouragement which has been given by Dr. Anson Hayes, Director of Research Laboratories, in carrying out this investigation, and in the assistance of Messrs. R. L. Solter and D. J. Fergus in preparing some of the micrographs.

DISCUSSION

Written Discussion: By O. W. Ellis, director, Ontario Research Foundation, Toronto, Canada.

The authors are to be congratulated on the perfection of so satisfactory a method for developing the austenitic grain size of eutectoid steel. The method should be invaluable to all who are interested in the investigation of steels of this general type.

The belief "that the austenitic grain size of steel is a function of the time and temperature to which the steel has been subjected, and cannot be predicted from tests that have been made on the steel when subjected to only one condition of time and temperature" is, of course, not new. The same thing has been expressed by other workers in other ways. Nevertheless, it is an opinion well worthy of the emphasis which has been placed upon it by the authors.

In this connection the writer, in a paper published in 1934 ("The Structure and Constitution of an Alloy Steel"—TRANSACTIONS, American Society for Metals, Vol. 22, p. 139-183), showed quite clearly the effect of maximum temperature and time of heating at maximum temperature, not merely on the austenitic grain size of an alloy steel (S.A.E. 3135), but also upon the struc-

tures resulting from cooling the steel from the maximum temperature at different rates (see, in particular, Fig. 17 of the writer's paper). An important conclusion resulting from this investigation, which might well be mentioned as a corollary to the authors' conclusion, was that "whatever the type of structure within the grains," subsequent to cooling, "their size appeared to be the same as for any given value of Θ max."

In the case of the S.A.E. steel examined by the writer, the effect of time of heating at maximum temperature was of vital importance only when the maximum temperature was below 1000 degrees Cent. (1830 degrees Fahr.); when the maximum temperature was above 1000 degrees Cent. (1830 degrees Fahr.), the rate of austenitic grain growth was so high that extending the time of heating from 15 to 130 minutes, for example, was without effect upon the final grain size of the steel.

The importance of maximum temperature was also brought out in the writer's paper on "The Behavior of Some Low Alloy Steels in the Single-Blow Drop Test" (TRANSACTIONS, American Society for Metals, 1937, Vol. 25 p. 826-841), in which the forgeability-temperature relationships for coarse-grained and fine-grained steels of approximately the same carbon content were discussed at some length. In this paper the interesting fact was brought out that the austenitic grain size of a steel shown by the McQuaid-Ehn test to be "coarse-grained" was actually finer at temperatures above about 975 degrees Cent. (1790 degrees Fahr.) than that of another steel of almost identical analysis, shown by the McQuaid-Ehn test to be "fine-grained." The effect of austenitic grain size upon the forgeability of these two steels is shown in Fig. 2 of the writer's paper. The results of these tests serve to support completely the conclusion of the authors, referred to in the second paragraph above.

The behavior of steel, whether to be heat treated or—one may add—to be plastically deformed, is therefore, as the authors have nicely shown, not to be arrived at by a study of its constitution under one set of time-temperature conditions. The characteristics of a given steel can in fact be expressed only in terms of three parameters—grain size, time, and temperature. Space models of the type prepared, for example, by Oberhoffer and Oertel, and reproduced as Fig. 8 by the senior author (Mr. Kenyon) in his article on "Effect of Plastic Deformation on the Physical and Mechanical Properties of Pure Iron" in the A.S.M. Metals Handbook, are required to cover all the variations in temperature, time, and grain size that are to be met with in practice when dealing with a single steel.

Written Discussion: By J. K. Stone and J. R. Vilella, Research Laboratory, U. S. Steel Corporation, Kearny, New Jersey.

The large number of well presented data showing the effect of time at temperature on austenite grain size is especially interesting to investigators who have been obtaining results in general agreement with those of the authors. The employment of the non-carburizing methods of determining austenite grain size is gratifying. The method outlined for determining the austenite grain size of a sample which has not been treated specifically to reveal the grain size, should find wide use, particularly for determining austenite grain size in heat treated steels either before placing in service or after removal therefrom.

We would like to raise a question as to the history of the steel investigated. Although its grain size characteristics seem to indicate that it is of the so-called "fine-grained," aluminum-treated variety, we would not expect an aluminum-treated steel to yield at all temperatures such uniform grain sizes as are reported. It is possible that the authors reported only average grain size values and we would like to ask if this is the case. Fig. 10 implies that all the samples showed a uniform grain size but a careful examination of, for example, Fig. 9F shows what we would call a sample of mixed grain size although the authors call it a uniform 5. If mixed grain sizes were encountered under certain conditions of time and temperature, it might have been more enlightening to report and plot them as such. Thus in Fig. 10 a plot of the percentage of the steel which had undergone coarsening against time at temperature might have given even a better representation of the true grain size behavior.

The data which show that a high temperature normalize, with its attending coarsened austenite grains, will produce no different effect upon subsequent grain growth behavior than does a lower normalizing temperature, with its attending finer austenite grains, is somewhat at variance with the majority of our experience with a limited number of steels. In some work, we were able to raise the coarsening temperature of steels by 100 degrees Fahr. by air cooling from 2000 degrees Fahr. or above.

We are of the opinion that some effect of heating rate upon austenite grain size would have been observed had the work been extended to include determination of austenite grain size within the coarsening range of the steel. A test in this range would be much more sensitive, thus increasing the likelihood of obtaining an effect due to the fact that now the steel would be on the verge of coarsening so that a small additional factor such as prior austenite grain size might coarsen it.

Although the data presented seem to show that rate of heating within the critical range (A_1 to A_3) has no effect on grain size, there is some evidence to indicate that heating rate through some other temperature range may be a factor. Thus, we have some data which tend to show that heating rate does change the austenite grain growth pattern and further that the rate of heating below the critical temperature is more important than that within the critical range.

We agree with the authors that the McQuaid-Ehn test has distinct limitations in predicting grain size behavior except for the given set of conditions under which it is conducted; in other words, that it yields only one point on a three dimensional Time-Temperature-Grain Size diagram of the steel as carburized. We fail to see why the term "inherent grain size" should be applied to that measured after any specific heat treatment, when in reality the value so obtained is only a measure of the grain size established by the specific heat treatment. If the word "inherent" has any place at all in grain size terminology, it should probably be in connection with "inherent grain size characteristics" which would depend not upon a particular heat treatment given a steel, but upon some characteristic property or set of properties built into the steel during the melting or deoxidation of the heat in question.

Written Discussion: By Oscar E. Harder, Battelle Memorial Institute, Columbus, Ohio.

The results of some researches which we have conducted on austenitic grain growth may be of interest in connection with this paper by Messrs. Tobin and Kenyon. I refer particularly to the effect of previous austenite grain sizes as discussed on page 139 of their paper. Some of our work is to be presented later on this same program.

The steel studied by Messrs. Tobin and Kenyon appears to have a rather low coarsening temperature thus suggesting that it contains relatively little of grain growth inhibiting material. The heat treatments selected by the authors to determine the effect of previous austenitic grain size do not appear to be the best ones possible to bring out certain differences. For example, both specimens were air-cooled from the preliminary heat treating temperatures whereas our work indicates that better contrasts are brought out if a comparison is made between quenched and slowly cooled materials.

To illustrate this point I shall discuss the results with the steel which we have designated as B-9, which contained a 0.35 per cent carbon, 0.80 per cent manganese, 0.022 per cent phosphorus, 0.024 per cent sulphur, 0.07 per cent silicon, 0.06 per cent chromium and which was aluminum-killed. Thus our

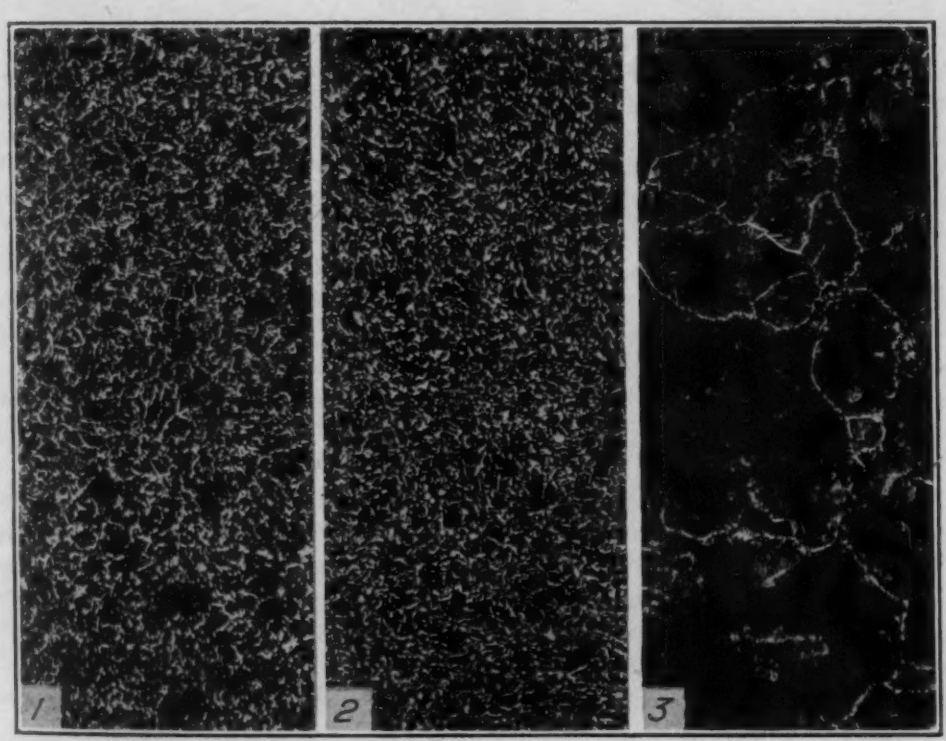

Fig. 1—B9-GB. Held at 2000 Degrees Fahr. for 1 Hour and Quenched in Water. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 2—B9-GB. Held at 2000 Degrees Fahr. for 1 Hour and Quenched in Water. Heated to 1500 Degrees Fahr. for 3 Hours and Quenched in Water. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

Fig. 3—B9-EB. Held at 2000 Degrees Fahr. for 1 Hour and Cooled 1½ Hours to 1500 Degrees Fahr. Held at 1500 Degrees Fahr. for 3 Hours and Quenched in Water. Heated to 1650 Degrees Fahr. for 1 Hour and Rapidly Cooled. × 100.

test was made on a hypoeutectoid steel. Photomicrographs from the paper by Dr. Dorn and myself will illustrate a difference which we obtain due to pretreatment. All of these specimens were given a coarsening treatment by heating at 2000 degrees Fahr. for one hour. Fig. 1 represents the microstructure obtained on a specimen which was quenched in water from 2000 degrees Fahr. and then reheated for grain coarsening at 1650 degrees Fahr. for one hour and rapidly cooled.

Fig. 2 represents the structure of a specimen which after quenching in water from 2000 degrees Fahr. was reheated at 1500 degrees Fahr. for three hours, quenched in water and then grain-coarsened at 1650 degrees Fahr. for one hour, followed by rapid cooling. Both of these specimens show relatively fine structures and there is essentially no difference.

Fig. 3 was similarly coarsened at 2000 degrees Fahr. but slowly cooled in one and one-half hours to 1500 degrees Fahr. held at that temperature for three hours and then quenched. It was then given a coarsening treatment by heating to 1650 degrees Fahr. for one hour as in the case of the other specimens.

It is obvious that Fig. 3 shows a much coarser grain size. This we interpret to mean that at the elevated temperature of 2000 degrees Fahr. the grain growth inhibiting material was largely in soluton. Slow cooling to 1500 degrees Fahr. resulted in the concentration of the grain growth inhibiting material at the boundaries of the large grains developed at 2000 degrees Fahr. The interior of these large grains under this condition contained relatively little of the grain growth inhibiting material. As a result when this specimen was reheated to 1650 degrees Fahr. the grains grew rapidly, not for lack of the steel containing sufficient grain growth inhibiting material, but due to this material being concentrated at the boundaries of the original coarse austenite grains and therefore ineffective to prevent grain growth. The grains tended to grow to the boundaries of the original coarse austenite grains.

In the case of the specimens which were quenched from 2000 degrees Fahr., our interpretation is that the grain growth inhibiting material was well distributed throughout the grains, probably as a supersaturated solid solution. As a result on reheating the austenite grains began to form and the grain growth inhibiting material was concentrated at their boundaries and tended to prevent them showing excessive grain growth.

Other conditions under which previous treatment influences the austenite grain size are discussed in the paper which is to be presented later.

While the authors have found a particular relation with the steel studied and the experimental procedure, there seems to be ample evidence that their findings are not general and will not hold for all steels and all methods of heat treatment. Perhaps even a eutectoid steel of somewhat different characteristics might not give the same results as found with this particular steel.

Oral Discussion

C. A. SIEBERT:[1] I was interested in this paper and in the discussion that followed, and I want to give an experience we have had in regard to austenitic

[1]Assistant Professor of Metallurgy, University of Michigan, Ann Arbor, Mich.

grain size. We have run experiments on four different steels, mostly in the S.A.E. 1020 class, and one was a low alloy steel. If it is true that the material inhibiting grain growth is in solution at the higher temperature, then we would expect that the samples cooled in the furnace from the high temperature would coarsen more easily. Our experience has been that there is no definite correlation.

We have found by running furnace cooling, air cooling, oil quenching and water quenching from high temperatures and then determining grain size again at say 1700 or 1750 degrees Fahr. that there is no definite correlation between the treatment and the grain size that you will expect. In one case you will find that possibly the oil quenching from the high temperature has given the condition that will cause coarsening of the grain to take place readily; in another case it may be the normalizing. So far in the steels we have examined we have found no definite correlation that we could say depended upon some certain rate of cooling.

Authors' Closure

The authors appreciate the interest shown in their paper by those who have offered discussions.

We should like to say first that we tried to emphasize in the title of the paper that our work was confined to eutectoid steels. We realize that there may be differences, great differences perhaps, between the behavior of eutectoid steels and the hypoeutectoid steels that apparently have received considerably more attention, in all of this grain size discussion and study that has been going on over a period of years, than the eutectoid steels. We have felt that this was probably due in some measure to the difficulty of determining the austenitic grain size of eutectoid steels. There has been no satisfactory means of delineating the grain boundaries thereof, and our primary attempt was just that—to work out some means of showing these grain boundaries.

In developing the method we have described, we performed experiments which we thought would be of value and interest along the lines of effect of heating and cooling rates and previous treatment. We presented these, however, as incidental to the main point of the paper, which is that steels have a characteristic grain growth behavior, and that this entire behavior must be studied in order to get a true picture of the austenitic grain size of the steel in question. The discussion by Mr. Ellis furnishes several interesting confirmations of this main point of our paper, and we welcome his contribution as a confirmation of our contentions.

Replying to some of the other comments that have been made, we would say with reference to the point brought out by Messrs. Stone and Vilella that the steel which we used was not aluminum-treated. It was a straight carbon steel without any special treatment, the hot-rolled strip being made in the conventional way.

We wish to point out the ambiguity of the terms "fine-grained" and "coarse-grained" not only in this discussion but in many metallurgical articles. It seems quite proper to use these adjectives to describe a particular piece of steel, treated in a particular way, to have a particular grain size, as revealed

by a fracture test or microscopic examination. However, current use of these terms has been extended, improperly we believe, to describe the behavior of steels to heat treatment, assuming that a given steel will have the same general behavior to all heat treatments. In other words, a "coarse-grained" steel will always be coarser than a "fine-grained" steel under any heat treating conditions to which the two steels may be subjected. This is not always the case, because different steels have different grain growth characteristics, and it is meaningless to use these terms to describe the behavior of a steel unless the conditions of time and temperature are specified also. The steel represented in Fig. 10 of the paper, for example, was "fine-grained" after some heat treatments and "coarse-grained" after others.

We have used average grain size throughout our discussion as specifically stated on the eleventh page of the paper, feeling that it was much easier to estimate the average size than to determine what percentage of this and that grain size was shown in the photomicrograph. Perhaps this does not tell quite as complete a story, but for most purposes it seems to be sufficient. It is gratifying to note that Messrs. Stone and Vilella have indicated their agreement with the authors in the matter of the characteristic grain growth behavior being variable with different treatments, and of the necessity of studying this over the whole range in order to tell what that behavior will be.

Dr. Harder has presented some data on the effect of certain treatments of hypoeutectoid steels which were aluminum-killed. This was an entirely different material from that with which the authors worked, and we would like to point out that this information, interesting as it is in itself, does not seem to controvert any of the statements which we have made. The effect of pretreatment on the austenitic grain size discussion in our paper refers only to eutectoid steels. Our data on the previous effect of austenitic grain size and rate of heating through the critical temperature were presented only as illustrations of applications that might be made of this method of metallographic preparation as a means of studying the austenitic grain size of eutectoid steels. The variation in grain growth behavior of different steels was clearly emphasized on the twelfth and thirteenth pages of the paper, and it is hoped that the methods described by the authors might prove a useful tool in carrying out the study of this behavior on a wide variety of steels.

Mr. Siebert's remarks also pertain largely to hypoeutectoid steels, but it is interesting to note his evidence that the cooling rates of the S.A.E. 1020 steels used in his investigation did not seem to be influential as far as the austenitic grain size was concerned.

SOME FACTORS INFLUENCING AUSTENITIC GRAIN SIZE IN HIGH PURITY STEELS

By G. Derge, A. R. Kommel and R. F. Mehl

Abstract

To determine the relative importance of aluminum in solid solution and finely dispersed Al_2O_3 in controlling the austenitic grain size of steels, high purity iron-aluminum samples were prepared by diffusing aluminum into hydrogen purified carbonyl iron. To obtain Fe-Al_2O_3 samples the iron-aluminum material was treated in hydrogen containing a small amount of oxygen. Additional samples were made by vacuum fusion of aluminum with purified and unpurified carbonyl iron. The same diffusion technique was used in preparing samples with silicon and SiO_2.

An oxygen free hydrogen-hydrocarbon gas was used to carburize the irons, and the grain growth characteristics of the resultant steels were determined.

The experiments showed that grain growth is inhibited by the refractory oxides, and that the magnitude of the effect is sensitive to the dispersion of the oxide.

Pack carburization of the same samples produced abnormal structures in all material, indicating that abnormality is due to oxygen in the carburizing gas rather than to oxides in the metal.

I. Introduction

WIDESPREAD interest in the control of austenitic grain sizes in steels has resulted in numerous studies of the methods of control, but no theory has been accepted as to why these methods work. The paper by Swinden and Bolsover (1)[1] and the accompanying discussion is representative of current thought upon the subject. One group of metallurgists believes with Bain (2) and Herty (3) that grain growth is inhibited by finely dispersed non-metallic particles such as carbides, nitrides, and refractory oxides. Another group, led by McQuaid (4), is of the opinion that metallic aluminum in solid

[1]The figures appearing in parentheses pertain to the references appended to this paper.

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. Of the authors, G. Derge is associated with the Metals Research Laboratory, Carnegie Institute of Technology, A. R. Kommel is associated with the United Engineering and Foundry Co., Vandergrift, Pa., and R. F. Mehl is Director of the Metals Research Laboratory and Head of the Department of Metallurgy, Carnegie Institute of Technology, Pittsburgh. Manuscript received June 25, 1937.

solution, through its influence on carbide behavior, restrains grain growth and gives rise to fine grained steels. Swinden and Bolsover do not subscribe to either of these views but think that the ultimate degree of deoxidation controls the grain growth characteristics; thus no general agreement has been reached on the problem.

Previous studies have been confined largely to commercial heats of steel, in which so many variables have operated that no clear-cut distinction could be drawn between the effects of aluminum in solid solution and aluminum as Al_2O_3. Recently Brophy and Parker (5) prepared high purity iron-aluminum alloys by vacuum melting and found them to possess normal pearlite structures when carburized in oxygen-free hydrocarbons but to be abnormal when pack carburized. The abnormality was attributed to the formation of Al_2O_3, but no grain size data were collected. Other evidence from aluminum-free steels (2), (6) indicates that abnormality is due to the presence of oxygen in solid solution rather than oxide, however, grain size and not abnormality is our immediate concern.

The present experiments were undertaken with the hope that additional information could be obtained by the use of high purity materials prepared and heated under carefully controlled laboratory conditions so that the few variables present would be definitely known. Iron-aluminum and iron-silicon alloys were prepared by diffusing aluminum and silicon into hydrogen purified carbonyl iron, thus avoiding any possible contamination with oxide particles from the refractory crucible required by any melting technique. After homogenization, these samples were bisected and half of them treated in a H_2-H_2O mixture containing enough H_2O to oxidize the aluminum or silicon but not the iron; after carburizing in oxygen free hydrogen-hydrocarbon gas mixtures the grain growth characteristics of these samples were determined. It was realized that this procedure, though highly desirable for many reasons, would probably result in a different dispersion of Al_2O_3 than that obtained by the usual melting practice. Therefore, additional samples were prepared by induction melting in vacuum.

II. Experimental Procedure

Hydrogen purified carbonyl iron, described in earlier papers from this laboratory (7), (8), (9) was used unless otherwise specified. Disks for the diffusion samples were cut $\frac{1}{16}$ to $\frac{1}{8}$ inch thick from a $\frac{3}{8}$-inch rod. High purity aluminum was used for the techniques of

vacuum melting and vaporization in hydrogen, while 99.3 per cent aluminum foil was used in electrodeposition. The silicon was reported as 99 per cent pure; the Fe_2O_3 was "C.P."

The hydrogen was electrolytic tank hydrogen which had been passed over a 3 foot by 1½ inch platinized asbestos catalyst, an alumina "Lectrodryer" with 100 cubic feet per hour capacity, and finally a BaO drying tube, 2 inches by 6 feet. All tubing was Pyrex glass, connections were made with gum-rubber boiled in NaOH. No indication of oxygen was found at any time on the samples used or on a stainless steel test piece (10).

The gas carburizing was done by the method already developed for the preparation of pure steels, by bubbling hydrogen through sulfur-free dipentene and benzene (9).

The furnaces were also of the design described in earlier papers (7), (9); the section containing the samples was a hydrogen purified Armco iron pipe.

During the homogenizing the aluminum diffusion samples were supported in a hydrogen-purified Armco iron tube with wire of the same material. Quartz tubing was used for the silicon samples. The center section of the carburizing furnace contained high purity magnesia tubes.

Aluminum was deposited successfully by two methods: (a) by vaporizing in hydrogen at 800 degrees, using a graphite crucible and enclosing the whole in a purified Armco iron pipe, and (b) by electrodeposition by the method of Blue and Mathers (11). The latter was more rapid and easier to control and was therefore used for the large majority of samples. Adherent coats were obtained when the samples had been given a preliminary etch with 2 per cent nital just before electrodeposition. The anhydrous nature of the electrolyte and the evolution of cathodic hydrogen during deposition seem to insure the formation of aluminum free from oxide. A few samples were prepared by vaporizing aluminum in vacuum; some of these were prepared for us by Mr. Brophy of the General Electric Research Laboratories and others were prepared by us. These vaporized films did not adhere well and study showed that they were at least partly oxidized so that the results obtained will not be reported.

Silicon was deposited by packing the samples in a quartz tube with lumps of silicon and passing pure hydrogen through the assembly at about 1200 degrees Cent.

The samples shown in Table IV were prepared by induction

melting in vacuum. The weighed materials were placed in a 50 cubic centimeters high-purity alumina crucible which was supported on another crucible within a larger glazed quartz tube which was connected to a vacuum system by a Picein sealed quartz-to-pyrex ground joint. The vacuum system consisted of a simple McCleod gage, a single-stage mercury diffusion pump and an oil fore-pump. Before and after melting, pressures of less than 0.5 microns were obtained, but during the melting the pressure rose to about 2 microns.

Unpurified carbonyl iron has been reported to contain 0.1 to 0.2 per cent oxygen (7) and it was felt that melts 1 and 3 should contain a dispersion of oxides comparable to that in fine-grained commercial steels, while melts 2 and 4 with excess iron oxide to flux the Al_2O_3 (15) should represent a partially killed steel. Melts 4 and 6 should contain the deoxidizers in metallic solid solution.

The samples coated with aluminum were annealed for diffusion in pure hydrogen in an iron tube for 42 days at temperatures above 1100 degrees Cent. To avoid excessive loss of aluminum by melting and vaporization the homogenization was started at 650 degrees and the temperature gradually raised to 1150 degrees over a period of 13 days. The samples coated with silicon were homogenized for a total of 59 days above 1100 degrees in a quartz tube furnace, through which hydrogen was passed.

After homogenization, spectrographic examinations were made at the outer surfaces and centers of each sample. These showed that aluminum and silicon had diffused into the center even though homogenization was not complete.

After the homogenization the samples were cut in half. One half of each was oxidized by passing pure hydrogen through three water saturators at room temperature and then into the furnace at 1100 degrees Cent. (2010 degrees Fahr.) for four days. The partial pressure of oxygen under these conditions is theoretically too low to oxidize any iron. (12) For the aluminum alloys this was followed by two days treatment with dry hydrogen to remove any oxygen from the iron.

The carburizing procedure adopted was to bubble 50 cubic centimeters per minute of pure dry hydrogen through dipentene at room temperature and then to pass it through the carburizing furnace at 1100 degrees Cent. (2010 degrees Fahr.) for 48 hours. As a rule the samples were estimated to contain about 0.4 per cent carbon after this treatment, though the variation was great. To avoid pos-

sible reduction of SiO_2, the carburizing gas for these samples was also passed through water saturators. Pack carburizing was done with Houghton's No. 50 Pearlite.

The heat treating schedule used to determine the grain growth characteristics was as follows: the carburizing furnace and gas were used to avoid any change of composition during the treatment. The samples were placed in an alundum boat which was placed in the cold end of the tube and attached to a wire which passed through the hydrogen outlet. When the furnace reached the desired temperature, the boat was pulled into the hot zone and then pulled through to the other cold end after one-half hour at temperature. The rapid cooling obtained in this way developed a satisfactory outline of ferrite around the austenite grains. The as-carburized samples were all given an initial grain refining treatment by passing through the critical range three times before determining the grain growth characteristics. Grain sizes were determined in this fashion at 800, 900, 1000, and 1100 degrees Cent. (1470, 1650, 1830, 2010 degrees Fahr.) by successive treatments of the same sample.

After each treatment grain sizes were determined and recorded according to the American Society for Testing Materials' grain size chart by standard metallographic methods. Examination of a few cross sections showed that after each stage of the process the samples were homogeneous throughout. Chemical analyses for Al_2O_3 were made to check upon the effectiveness of the procedures described for producing samples which were either oxidized or not oxidized. The HCl residue method (13) for the determination of Al_2O_3 in steels was used, as it is far simpler than the iodine or vacuum-fusion methods and has been shown to give results comparable to them. (14) The residues were tested qualitatively for aluminum by both the $Al(OH)_3$ and "aluminon" tests and gave positive results. It was necessary to use small samples of about 1 gram, so no test was made for additional elements in the residue and the filtrate was not examined further. The results listed in Table I are considered to give definite proof that only those samples which had been oxidized contained Al_2O_3. No difference of particle size was apparent in these residues. The analyses of the melts were made on uncarburized specimens, but the diffusion samples had been through the entire gamut of homogenization, carburization, and heat treatment. At this time a negligible amount of oxide was present in the unoxidized material.

Table I

Sample	Remarks	Residue
Melt #1	0.1 Per Cent Aluminum + unpurified carbonyl iron, vacuum melted	0.15
Melt #4	0.1 Per Cent Aluminum + Fe_2O_3 + unpurified carbonyl iron, vacuum melted	0.10
Melt #5	0.1 Per Cent Aluminum + H_2 purified carbonyl iron, vacuum melted	0.00
Blank	H_2 purified carbonyl iron, as used	0.00
U-D 2	Aluminum-iron diffusion sample, oxidized, carburized, and heat treated	0.15
D 2	Aluminum-iron diffusion sample, not oxidized, carburized and heat treated	0.03

III Experimental Results

The grain sizes of the aluminum and Al_2O_3 samples prepared by diffusion are shown in Table II. Measurements were not carried beyond 1000 degrees Cent. (1830 degrees Fahr.) as coarsening had started at this temperature in all samples. The contrast in grain size between the unoxidized and oxidized sections is not as great as that observed between fine- and coarse-grained heats in commercial practice. However, it should be remembered that grain size numbers represent a geometrical progression and the differences noted are appreciable and definite. It may also be remarked that these samples show the intermediate grain sizes which cannot be obtained readily in commercial practice. A typical set of micrographs is shown in Figs. 1 to 6.

Table III gives the data obtained from the silicon and SiO_2 samples. After the grain refining and heat treatment at 800 degrees Cent. (1470 degrees Fahr.) the oxidized samples showed a much finer grain than the unoxidized. The 900 degrees treatment showed that appreciable grain growth had occurred in all samples. This substantiates the belief that SiO_2 inhibits grain growth, but only at low temperatures.

Table IV gives the data obtained from the samples prepared by vacuum melting. Melts 1 and 3 containing Al_2O_3 behave as commercial fine-grained steels. The second set of values at 800 and 900 degrees Cent. (1470-1650 degrees Fahr.) was taken after the treatment at 1100 degrees Cent. (2010 degrees Fahr.) which coarsened the steel. The other melts (oxide-free) act as coarse-grained steels. Typical photomicrographs are shown in Figs. 7 to 13.

Several of the steels were recarburized until hypereutectoid as abnormality would be more easily observed under these conditions. Some were carburized in oxygen-free hydrocarbon gas and showed normal structures only, see Fig 14. Others were pack carburized

and these showed very definite abnormality, as is illustrated by Fig 15. To avoid any possibility of attributing the abnormality to the pres-

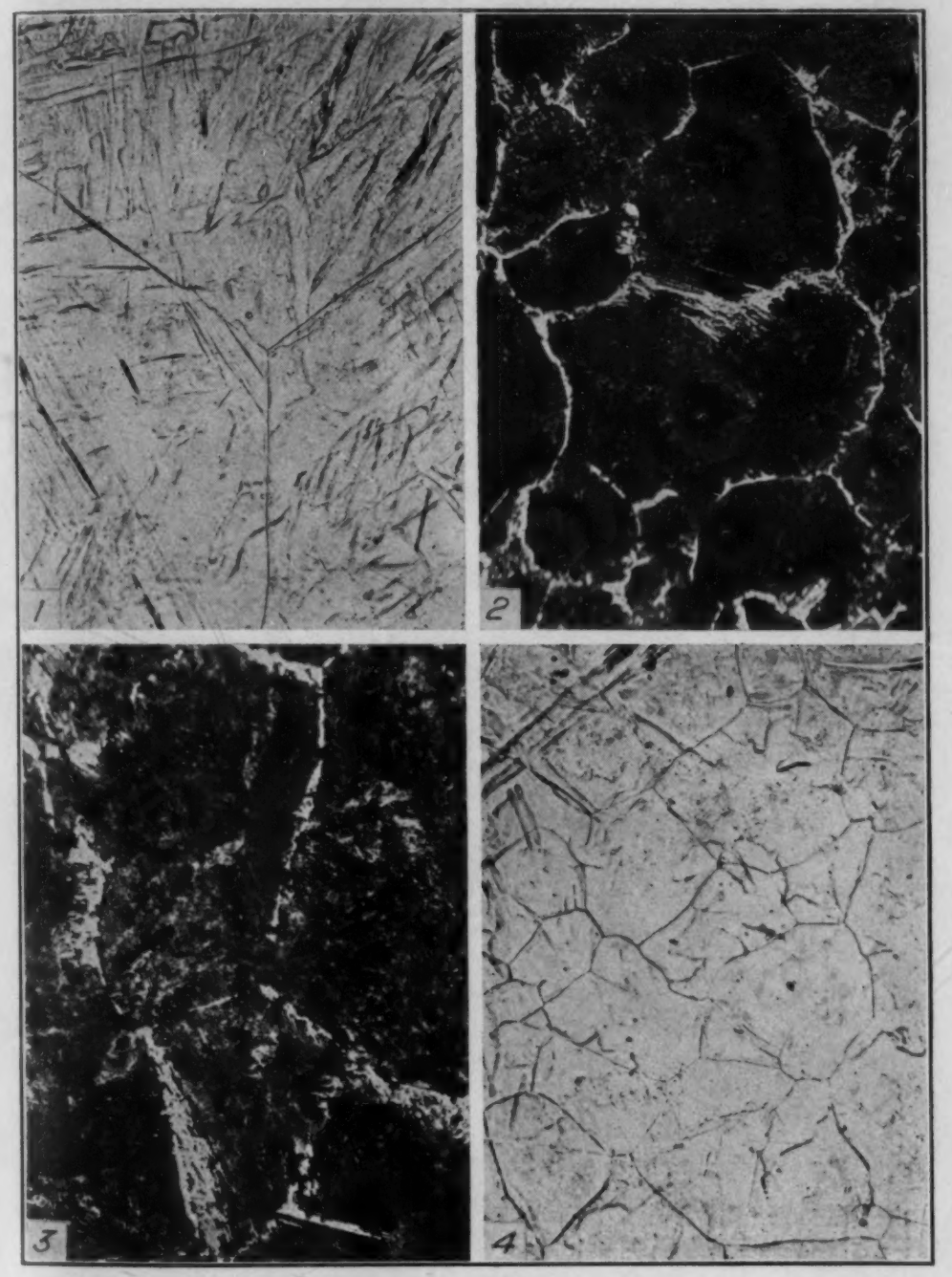

Fig. 1—D-7, As-Carburized. Heat Etched in Carburizing Gas. × 100.
Fig. 2—D-7, After One-Half Hour at 900 Degrees Cent. (1650 Degrees Fahr.). Nital Etch. × 100.
Fig. 3—D-7, After One-Half Hour at 1000 Degrees Cent. (1830 Degrees Fahr.), Nital Etch. × 100.
Fig. 4—UD-7, As-Carburized. Heat Etched in Carburizing Gas. × 100.

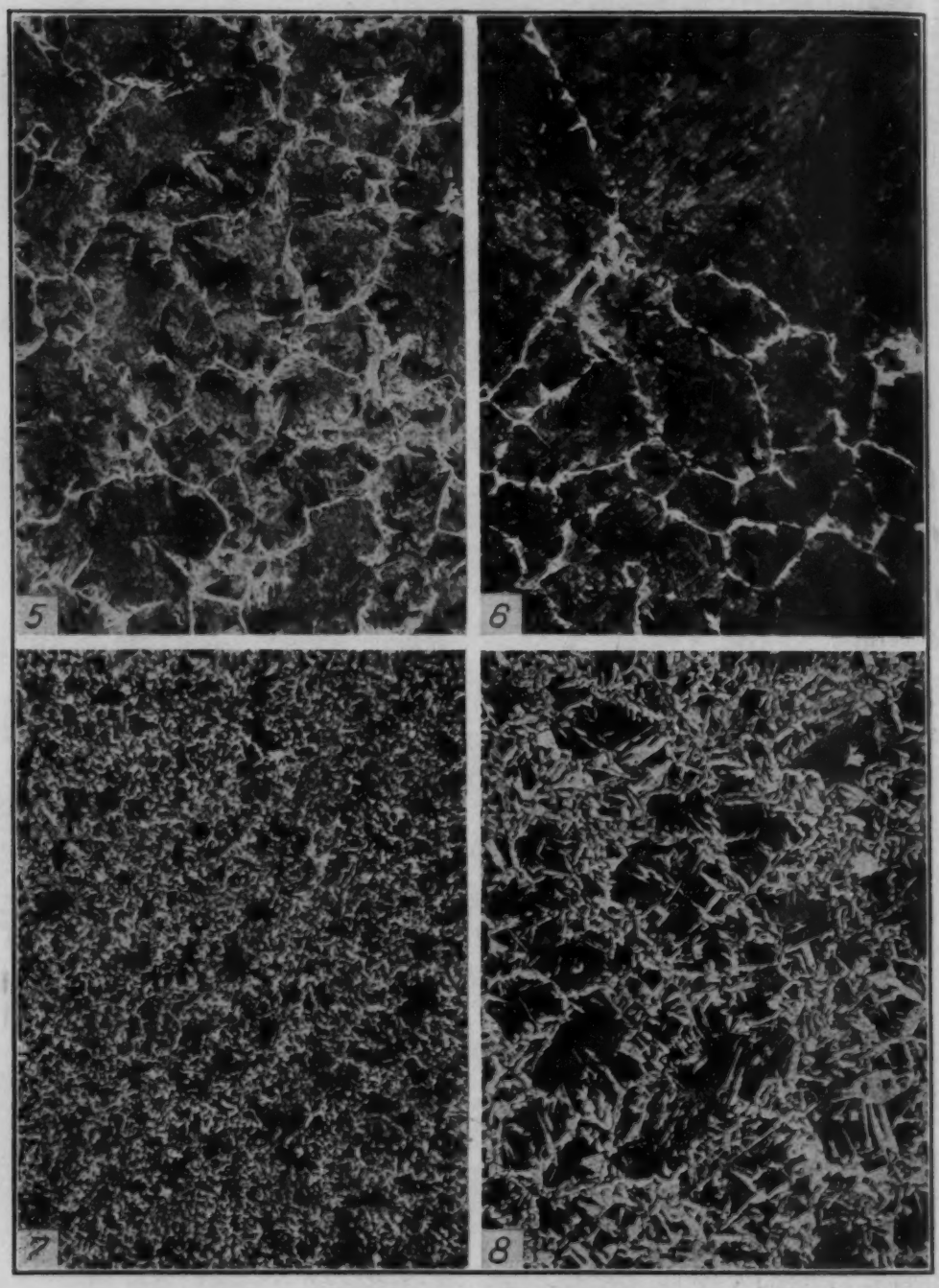

Fig. 5—UD-7, After One-Half Hour at 900 Degrees Cent. (1650 Degrees Fahr.), Nital Etch. × 100.

Fig. 6—UD-7, After One-Half Hour at 1000 Degrees Cent. (1830 Degrees Fahr.), Nital Etch. × 100.

Fig. 7—Melt 5, After One-Half Hour at 800 Degrees Cent. (1470 Degrees Fahr.), Nital Etch. × 100.

Fig. 8—Melt 5, After One-Half Hour at 900 Degrees Cent. (1650 Degrees Fahr.), Nital Etch. × 100.

Table II

Sample	Composition	As Carburized	Grain Size Degrees Cent. 800	900	1000
C-3	0.2 Per Cent Aluminum added by vaporization in hydrogen and diffusion.	coarser than —3	5	2	2
UC-3 (oxidized)		0	5	3	3*, 0
D-2	0.15 Per Cent Aluminum added by electrodeposition and diffusion.	2	4	3	1
UD-2 (oxidized)		0	6-3	4	3
D-7	0.07 Per Cent Aluminum added by electrodeposition and diffusion.	coarser than —3	..	1	1, —1
UD-7 (oxidized)		2	..	3	2*, 0

*Predominating grain size.

Table III

Sample	Composition**	As Carburized	Grain Size 800 Degrees Cent.	900 Degrees Cent.
S-I	0.048 Per Cent Silicon	—3	3	2
X-I (oxidized)		—4	4-5	2-3
S-XII	0.32 Per Cent Silicon	—3	3	2
X-XII (oxidized)		3	5	3-4
S-G2	0.19 Per Cent Silicon	—3	4	2
X-G2 (oxidized)		1 to —3	6	1
S-G6	0.10 Per Cent Silicon	—3	2*, 1	1
X-G6 (oxidized)		1 to —4	6	3

*Predominating grain size.

**The silicon of all these samples was added by vaporization in hydrogen and diffusion.

Table IV

Sample	Remarks	Grain Size Degrees Cent. 800	900	1000	1100
Melt 1	0.1 Per Cent Aluminum, Carbonyl Iron	7 6	6 7*, 3	6*, 3	1, —1
Melt 3	0.1 Per Cent Aluminum, 0.04 Per Cent Silicon, Carbonyl Iron	7 6	7 7*, 3	6, 4	1*, 5
Melt 5	0.1 Per Cent Aluminum, H_2 purified carbonyl iron	6	3	2, 3	
Melt 6	0.1 Per Cent Aluminum, 0.03 Per Cent Silicon, H_2 purified carbonyl iron	7	3	2, 3	
Melt 2	0.1 Per Cent Aluminum, 0.04 Per Cent Silicon, Fe_2O_3†, Carbonyl Iron†	7*, 4	2	1	
Melt 4	0.1 Per Cent Aluminum, Fe_2O_3†, Carbonyl Iron	7*, 3	2, 3	1	

*Predominating grain size.

†Enough Fe_2O_3 was added to oxidize all of the aluminum and silicon, neglecting the oxygen already present in the carbonyl iron.

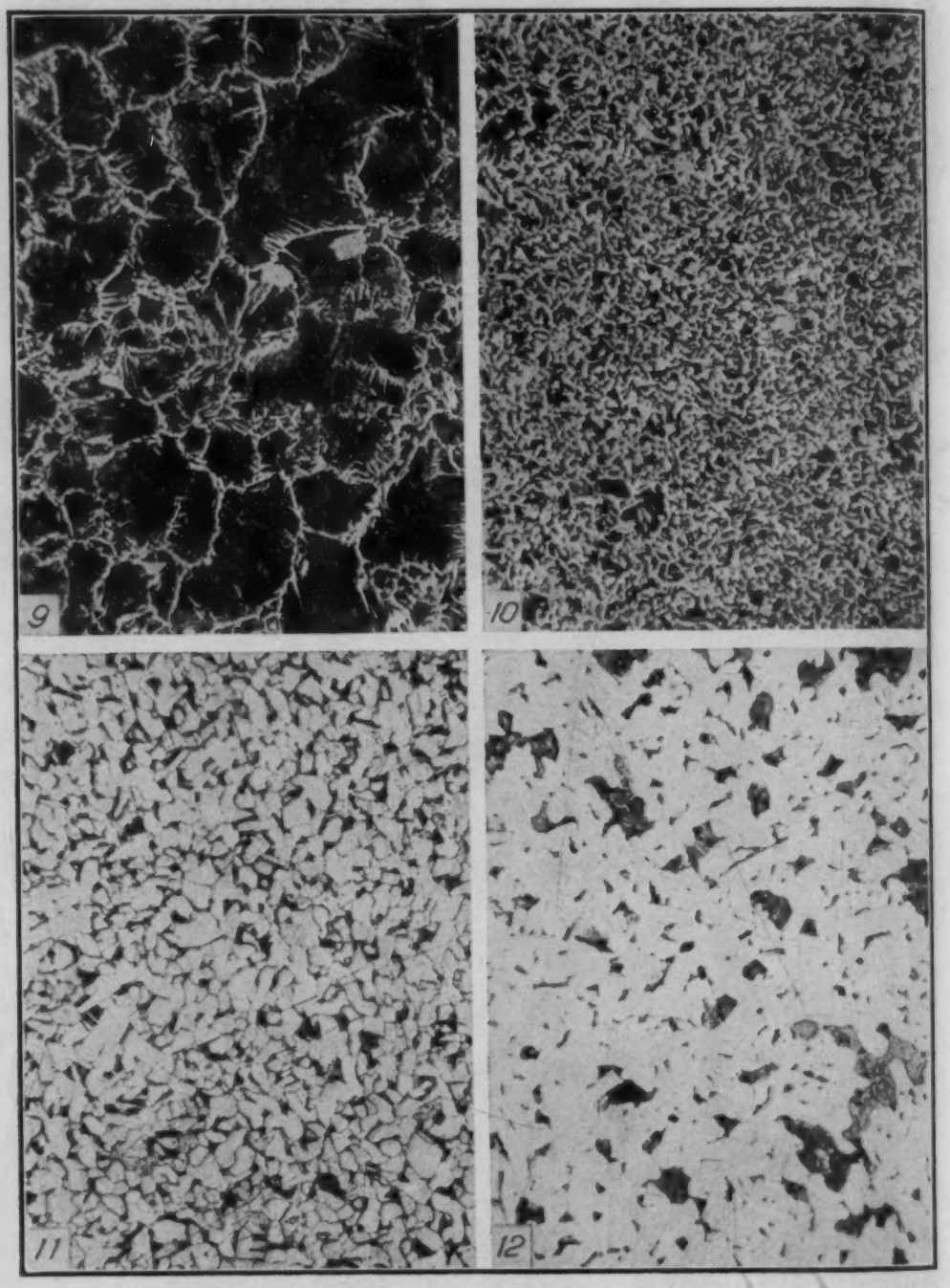

Fig. 9—Melt 5, After One-Half Hour at 1000 Degrees Cent. (1830 Degrees Fahr.), Nital Etch. × 100.

Fig. 10—Melt 1, After One-Half Hour at 800 Degrees Cent. (1470 Degrees Fahr.), Nital Etch. × 100.

Fig. 11—Melt 1, After One-Half Hour at 900 Degrees Cent. (1650 Degrees Fahr.), Nital Etch. × 100.

Fig. 12—Melt 1, After One-Half Hour at 1000 Degrees Cent. (1830 Degrees Fahr.), Nital Etch. × 100.

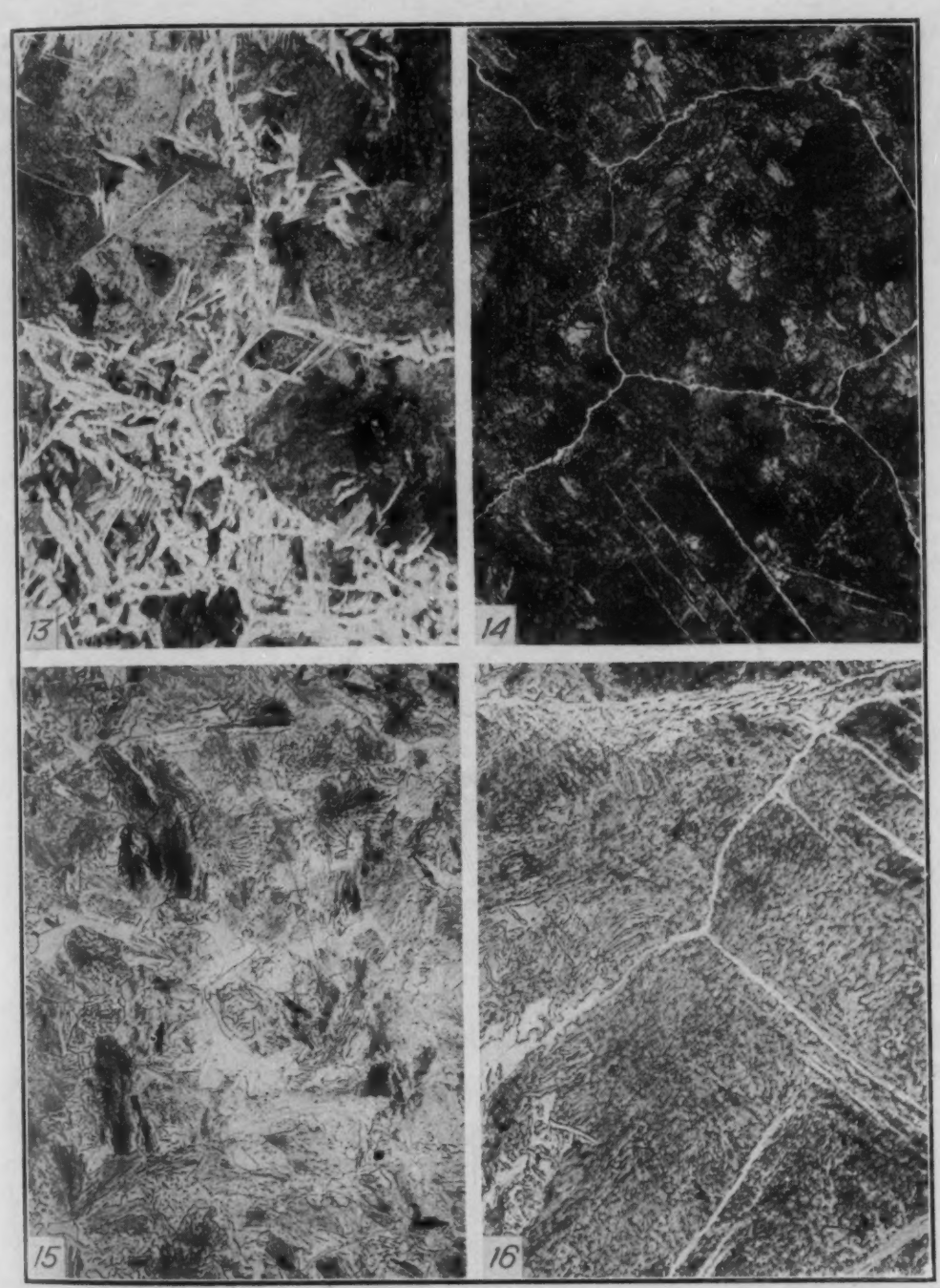

Fig. 13—Melt 1, After One-Half Hour at 1100 Degrees Cent. (2010 Degrees Fahr.), Nital Etch. × 100.

Fig. 14—D-7, Hypereutectoid Structure Developed by Gas Carburizing 48 Hours at 925 Degrees Cent. (1700 Degrees Fahr.), Nital Etch. × 100.

Fig. 15—UD-7, Hypereutectoid Structure Developed by Pack Carburizing. 48 Hours at 925 Degrees Cent. (1700 Degrees Fahr.), Nital Etch. × 100.

Fig. 16—Melt 1, Gas Carburized 48 Hours at 925 Degrees Cent. (1700 Degrees Fahr.), Nital Etch. × 250.

ence or formation of Al_2O_3, two samples of melt 1, containing the proper dispersion of Al_2O_3 for the formation of fine-grained steel, were treated as above. The normal gas-carburized structure is shown in Fig. 16, while the abnormal, pack-carburized specimen is shown in Fig. 17. These experiments all indicate that abnormality is due to the presence of oxygen and not aluminum or Al_2O_3.

Fig. 17—Melt 1, Pack Carburized 48 Hours at 925 Degrees Cent. (1700 Degrees Fahr.), Sodium Picrate Etch. × 250.

IV. Conclusions

The experimental results just described support the belief that finely dispersed solid particles inhibit austenite grain growth. They show further that Al_2O_3 or SiO_2 alone have this action and that a combination, such as an aluminum silicate, is not necessary. The effect of these refractory particles seems to be quite sensitive to their mode of dispersion; when the oxide was formed in the solid state by oxygen penetration, medium-grained steels resulted in the melted samples in which the oxygen present was just sufficient for the aluminum, a fine dispersion would be expected and this has given fine-grained steels. However, with excess oxygen present, a coarser dispersion may be expected due to the fluxing action of FeO and this results in a coarse-grained steel.

No case of abnormality was observed in the specimens carburized in the hydrogen-hydrocarbon gas, which shows that oxide particles alone or aluminum in solid solution do not give rise to abnormality; it is necessary to have oxygen in solid solution in the iron.

These results are all in agreement with the hypothesis that fine-grained austenite is the result of inhibition of grain growth by properly dispersed insoluble particles.

V. Summary

1. High purity irons containing aluminum have been prepared by diffusion of electrodeposited aluminum.

2. High purity irons containing Al_2O_3 were prepared by oxidation of the irons containing aluminum.

3. Similarly, irons containing silicon and SiO_2 were prepared.

4. High purity irons containing aluminum and Al_2O_3 in different states of dispersion were prepared by induction melting in vacuum.

5. These samples were gas carburized and their grain growth characteristics determined.

6. The results lead to the conclusion that Al_2O_3 and SiO_2 inhibit grain growth; whereas aluminum and silicon in solid solution do not, and that the degree of inhibition is closely related to the type of dispersion of the oxides.

7. None of the gas-carburized samples showed abnormal structures.

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DISCUSSION

Written Discussion: By H. W. McQuaid, metallurgist, Republic Steel Corporation, Cleveland.

This paper discusses a subject which has been of particular interest to me for many years. I certainly want to correct the impression which this paper gives that I do not believe that grain growth is inhibited by finely dispersed nonmetallic particles such as carbides, nitrides and refractory oxides. Nothing could be farther from the truth. There is no doubt at all in my mind but what these play an important part in austenite grain growth. I am quite convinced that both carbides and nitrides are a very important factor, not only in controlling austenite grain size but also in determining grain growth ranges and hardenability characteristics. I believe, moreover, that these carbides and nitrides exert an influence not because of a uniform dispersion of submicroscopic particles but by their arrangement and precipitation in austenite boundaries. The effect of nitrogen in combination with aluminum on the austenite grain boundary as suggested by Benedicks and Löfquist, I believe is an important factor in determining the size of the austenite grain.

What I do not believe is that submicroscopic particles of an exceedingly stable oxide such as aluminum oxide is an important factor in determining the austenite grain size and grain growth ranges because of its uniform dispersion throughout a heat of steel. It seems difficult for me to believe that such a theory could have very much merit.

It is quite evident that this paper records the results of a most carefully planned and conducted investigation. In my opinion, however, the conclusions which the writers have drawn from the results obtained are not warranted by the data given. In the first place, Table II does not indicate to me that we should draw any other conclusions than that the grain size was only slightly affected by the oxidation of pure iron containing added aluminum. In my opinion it is difficult to rate grain size variation by single number on the A.S.T.M. chart and a variation of one number due to oxidation can hardly indicate an important effect because of the presence of oxidized aluminum.

The same criticism can be made in regard to the conclusion from Table III, that SiO_2 inhibited austenite grain growth.

The conclusion from Table IV, that melts No. 1 and No. 3, containing aluminum oxide, were fine-grained because of aluminum oxide is also, in my opinion, not warranted by the results. Are we to assume that in melts No. 2 and No. 4 the oxidized aluminum and silicon would not have any effect on

the grain size? It would seem to me that melts No. 2 and No. 4 might be taken to indicate that the absence of metallic aluminum or silicon resulted in a coarser grain in spite of the presence of oxidized aluminum and silicon. Melts No. 1 and No. 3, with metallic aluminum and silicon present and perhaps less aluminum oxide than melts No. 2 and No. 4, were very definitely finer in grain and certainly showed a much greater difference than between any heats given in Table II. Those who have been faced with the problem of producing the extremely fine-grained "abnormal" type of steel are quite familiar with the fact that there must be an excess of unoxidized aluminum in order to obtain satisfactory resistance to grain growth in the austenite. This fact is very well established as is the fact that when just enough aluminum is added to react with the oxide available in a well killed heat that the steel will not be of the very fine-grained type nor will it be of the "abnormal" type which is required by some steel users.

Table IV might be considered to indicate that hydrogen has an important effect in promoting austenite grain coarsening, and this thought seems to me to warrant some attention. All of the tests which I have made indicate that it is not the absence of oxygen which makes steel carburized in a hydrogen-hydrocarbon mixture coarser grained and "normal," but rather the presence of hydrogen. Steels melted under hydrogen and carburized at an extremely slow rate in atmospheres of hydrogen-hydrocarbon will generally be found to be "normal" and coarse-grained in spite of aluminum oxide or heavy aluminum additions. Steels which would be fine-grained when tested in the usual way would be found to be fine-grained when melted under neutral atmospheres which excluded oxygen and hydrogen.

It has been my experience that silicon is an important factor in the results obtained after carburizing and also an important factor in the results which are obtained by aluminum additions. Apparently, silicon and hydrogen both act in some way to reduce the diffusion rate of iron carbide in ferrite at temperatures just below the Ac_1 and silicon, especially, promotes hardenability by its effect in producing pearlitic structures in which the carbide plates are more closely spaced and much thinner in section than when the silicon is low or absent. In no discussion of this sort can we eliminate the effect of hydrogen or silicon in promoting coarse-grained and "normal" structure. It seems to me that the aluminum addition is effective primarily in overcoming the stabilizing effect of silicon and hydrogen on the carbides in ferrite at temperatures just below the Ac_1 and that any addition of aluminum above the amount necessary to do this has little effect on the fineness of the austenite grain or the normality.

Written Discussion: By T. G. Digges, National Bureau of Standards, Washington, D. C.

The results of some work carried out at the National Bureau of Standards with high purity iron-carbon alloys are in agreement with the results of the authors in that abnormal structures were produced in these alloys which were free from both aluminum and alumina.

The preparation of these alloys has been described in some detail in a paper[1] presented at this convention. Essentially, the procedure consisted of

[1]Thomas G. Digges, "Effect of Carbon on the Hardenability of High Purity Iron-Carbon Alloys," Preprint No. 3, American Society for Metals, Oct. 18 to 22, 1937.

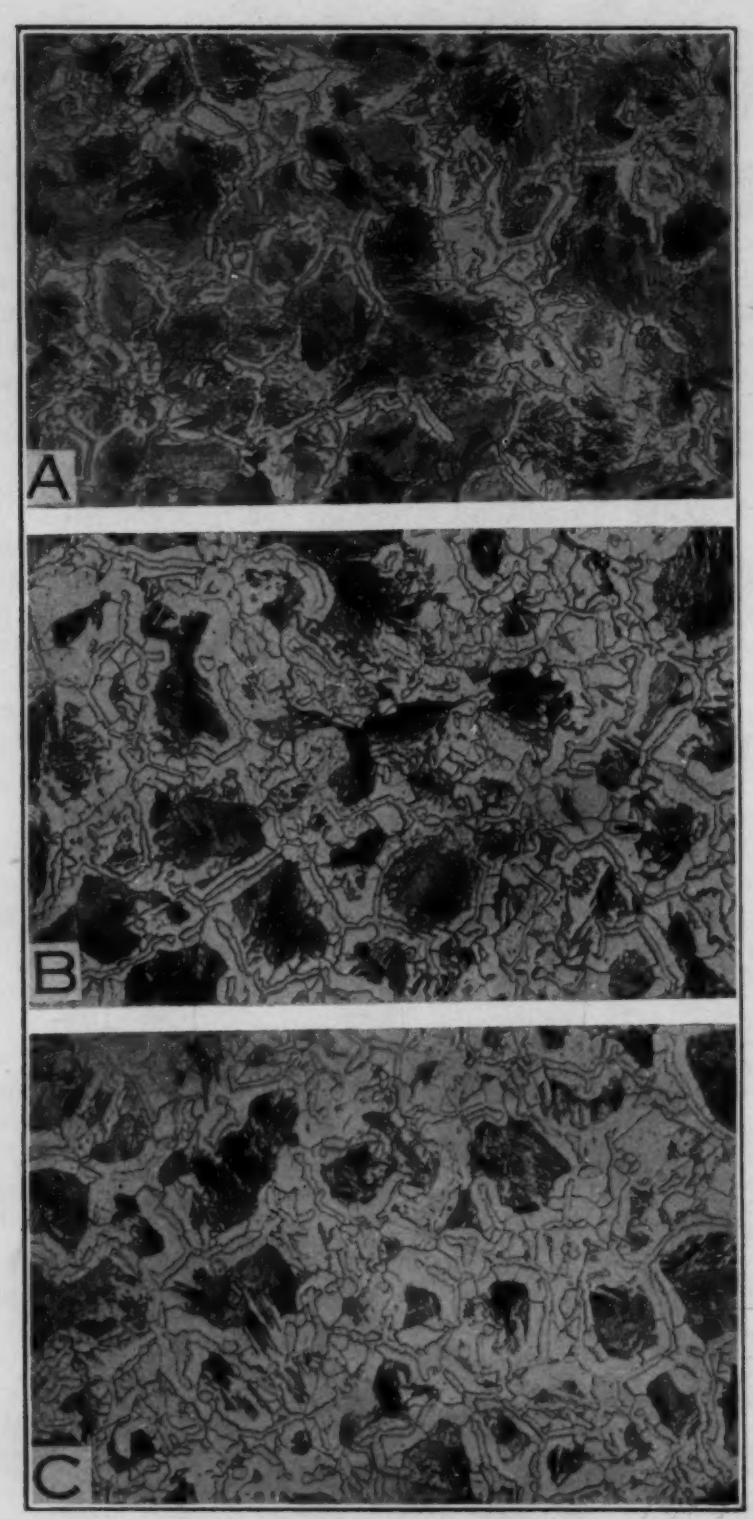

Fig. 1—Structure of High Purity Iron-carbon Alloys Annealed in Vacuo at 1700 Degrees Fahr. × 100. Etched with equal parts of nitric acid (1 per cent) and picric acid (5 per cent) in alcohol.

Fig. 1A—1.01 per cent Carbon. Fig. 1B—1.14 per cent Carbon. Fig. 1C—1.21 per cent Carbon. Photomicrographs by H, K. Herschman of the National Bureau of Standards.

carburizing hot- and cold-worked specimens of high purity iron in a mixture of hydrogen and benzine and subsequently homogenizing by heating in vacuo at 1700 degrees Fahr.

The structures produced in specimens of the hypereutectoid alloys containing 1.01, 1.14 and 1.21 per cent carbon, respectively, by slowly cooling in vacuo from 1700 degrees Fahr. are shown in Fig. 1 of this discussion.

These structures are distinctly abnormal as evidenced by the coalesced masses of cementite partially or entirely surrounded by ferrite. As shown in Table I, a small amount of oxygen (0.003 per cent by weight, analysis by vacuum-fusion method) was one of the impurities determined in similarly prepared specimens of the iron-carbon alloys.

It is of particular interest to observe that Bain[2] produced an almost entirely normal structure in a high purity iron containing a similar amount of oxygen (0.003 per cent) by carburizing in pure hydrogen and hydrocarbon. However, the iron used in Bain's experiment contained 0.028 per cent manganese as compared with 0.002 per cent in the alloys prepared at the National Bureau of Standards and reported in Table I.

Table I
Impurities Determined in the Iron-Carbon Alloys

Element	Analysis[1] (per cent by Weight) Spectrochemical[2]	Chemical	Vacuum Fusion
Manganese	.....	0.002	.....
Phosphorus	.....	less than 0.001	.....
Sulphur	.....	0.004	.....
Silicon	0.001	0.002	.....
Copper	less than 0.001	not detected	.....
Nickel	0.006	0.007	.....
Cobalt	.....	0.007	.....
Calcium	less than 0.001	.....	.....
Lead	probably less than 0.001	.....	.....
Magnesium	less than 0.001	.....	.....
Oxygen	.....	.....	0.003
Nitrogen	.....	.....	0.001
Hydrogen	.....	.....	0.0002

[1]Determinations were made on specimens from the bars after carburizing and heat treatment for homogeneity except as follows. Values of nickel, cobalt, and copper by chemical analysis were obtained from the electrolytic iron prior to melting and the values of manganese and phosphorus by chemical analysis were obtained from the bars as carburized. Spectrochemical analyses were made by B. F. Scribner, chemical analyses by W. H. Jukkola and J. L. Hague, and vacuum fusion analyses by V. C. F. Holm, all members of the staff of the National Bureau of Standards.

[2]Spectrum lines of cobalt and manganese were also found.

Advice from the authors whether in their opinion the higher manganese in iron used by Bain serves a role similar to the aluminum additions in the authors' specimens in preventing abnormality would be appreciated. If abnormality is produced by dissolved oxygen, would the small proportions present in the alloys used by the writer be sufficient to cause the marked abnormality shown in Fig. 1?

[2]Edgar C. Bain, "Factors Affecting the Inherent Hardenability of Steel," TRANSACTIONS American Society for Steel Treating, Vol. 20, November 1932, p. 385-428.

Oral Discussion

FRANCIS B. FOLEY:[3] I should like to suggest that this matter of grain size may be almost wholly chemical rather than physical; that is to say, we may not be dealing with mechanical obstructions offered to grain growth by non-metallic particles, such as alumina, nor with their effect when acting as crystal nuclei. The whole subject may be tied up in a chemical way with the solution and diffusion of metallic compounds, or even of gaseous molecules in the matrix of the steel above its critical temperature. We are dealing with the grain size of austenite. Austenite, when first formed, constitutes a solvent for the carbides that are present. This solvent, austenite, can be changed, let us say, by some addition that is made to the steel, such as nickel, silicon or aluminum. We may thus have, on the one hand, an austenite which is a good solvent and a carbide which readily decomposes and goes into solution and, on the other hand, we may by proper additions produce a very poor solvent together with a highly insoluble carbide. As long as the carbide, or oxide, is passing into solution in the austenite, it is possible that no grain growth can take place, because of disturbance of the lattice by the dissolving carbides, the metallic atoms of which are replacing iron atoms in the lattice and the carbon is finding a place in the lattice interstices. If the carbides quickly decompose and pass rapidly into solution grain growth starts early, whereas, if they are slow in passing into solution, grain growth is retarded. If the compound is entirely insoluble it should have practically no effect in retarding grain growth. A study of the effect of added elements and also of oxygen, hydrogen and nitrogen on the rate of solubility of carbides in austenite might lead to some very interesting information concerning grain growth. Bain, in his recent work, has shown that vanadium produces fine grain, due to the fact that the crystals do not start growing appreciably until the carbides are totally dissolved in the austenite.

I can conceive that abnormality and normality in steels could be accounted for by diffusion if it be supposed that during carburizing carbon penetrates most rapidly through grain boundaries and that from the grain boundaries diffusion takes place more slowly into the body of the crystal. If, due to the presence of some alloying element, the austenite which makes up the body of the crystal retards the progress of the carbon atoms into it, a hypoeutectoid crystal is surrounded by an enriched layer of carbon. Upon cooling, this hypoeutectoid center gives up ferrite, and the carbon in the boundaries combines to form carbide and gives an abnormal structure characterized by a carbide rim with excess ferrite surrounding the pearlite grains within.

Authors' Reply

DR. DERGE REPLIES: The discussions of this paper are very much appreciated, for those of us who work in a research laboratory are keenly aware that an unrestrained interchange of ideas between various laboratories, especially between the academic and industrial laboratories, is a prerequisite to the solution of metallurgical problems.

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[3]Superintendent of Research, The Midvale Company, Philadelphia.

Indeed it was Mr. McQuaid's Campbell Memorial Lecture which initiated the research which has just been reported. The summary of this lecture concludes that, "An hypothesis is offered suggesting metallic aluminum in solution and its effect on carbide coalescence as a cause of grain growth inhibition and pearlite divorce." We must apologize to him for any misrepresentation of his opinion which has resulted from removing this statement from its context.

As to whether or not our conclusions are justified, I feel that there is very little we can say. Our experimental evidence has been presented and others must decide whether or not this should carry any weight. We thought that the data showed consistent differences which could not be attributed to experimental error.

What I would like to call attention to, is that these experiments were performed with extreme care under controlled laboratory conditions so that a large number of uncertain variables are not present, as is usually the case in commercial practice. We feel that those differences which do appear in our data must be attributed to the fact that one set of samples contained aluminum, while the other contained aluminum oxide. The action of hydrogen, silicon, nitrogen, or any other element or combination of elements must have been the same on all the samples described. All treatments were identical, usually simultaneous, for both series of samples. I feel that within the limits of experimental technique which are available today, our specimens represent the difference between the effect of aluminum and of aluminum oxide, and that it would be dangerous to draw any other conclusion whatsoever.

The abnormality shown by the specimens of Mr. Digges certainly confirms the opinion we have expressed, which is only a repetition of that of other people, such as Brophy, that abnormality cannot be due to the presence of aluminum oxide alone but must be due to the presence of oxygen in the carburizing mixture, or some other influence. I think the whole question of abnormality is one of relative rates, as Mr. Foley brought out, and that there are undoubtedly a good many factors which can influence abnormality.

I do not believe it is safe to say, however, that our steels have been made normal, due to the presence of aluminum. The pure steels without any aluminum or aluminum oxide addition have been worked over very carefully in our laboratory by Dr. Wells in a series of carburizing experiments which have already been described in the literature, and in no case in which he used pure hydrocarbon mixtures without any oxygen did he find any abnormality. His structures in the pure steels containing no aluminum were just as normal as the structures in our steels containing aluminum. Consequently we cannot say whether or not the manganese in Bain's steels had any direct effect upon their normality. It may have an influence but I do not believe it has been established as yet, and a great deal more experimental work would be required to do so. The safest guess I can make as to Mr. Digges' abnormality is that it is due to oxygen which may have entered during his vacuum treatment. Of course it would also require very careful experimental work to determine whether or not enough oxygen entered to cause these effects. His structures are rather puzzling in comparison to the structures which Wells has obtained on steels which are certainly of comparable purity.

In regard to Mr. Foley's discussion, I would like to state that Dr. Wells

is now doing work in our laboratory which indicates that, in high purity steels at least, you cannot assume any more rapid diffusion of carbon in the grain boundaries than through the matrix of the grain. There does not seem to be any evidence to indicate that this is true. Undoubtedly in ordinary commercial steels there are segregations of impurities and other resultant effects, strains, etc., at the grain boundaries and there may be differences of diffusion rates there, but it would seem that in high purity steels carbon diffuses through the grain boundary at the same rate as it does through the bulk of the grain.

THE RATE OF AUSTENITE TRANSFORMATION IN CAST IRON

By D. W. Murphy, W. P. Wood and D. Girardi

Abstract

Further studies in the resolution of the austenitic grain size in cast iron are reported. The macro grain size pattern appears to be a trace of a condition arising soon after solidification is complete. A fine network structure representative of the austenitic grain size on reheating and outlined by nodular troostite has been developed. The macro and micro network structures seem to be parallel in a given series, i.e., irons of coarse macro network pattern show also the coarse micro pattern.

It is shown that the differences between the hardened structures of deep and shallow hardening cast irons are associated with wide differences in austenitic transformation rates. The fine-grained, shallow hardening irons transform considerably faster at 1000 degrees Fahr. than do the coarse-grained, deep hardening types. In general, the rate of transformation of austenite at 1000 degrees Fahr. is much slower than that for plain carbon steel.

IN previous papers[1, 2] the authors have presented data to show the influence of an austenitic grain size on the as-cast properties of gray cast irons and the influence of melting and deoxidation practice on hardenability and some additional physical properties. The first paper described four cupola heats and two induction furnace heats; the cupola metal was cast as small rectangular bars whose maximum cross section was ⅜ by ⅛ inch while the induction furnace irons were cast into bars about 1 inch in diameter. Analyses of the cupola irons which were used to show the influence of varying grain size on physical properties were sufficiently close in the commonly determined elements of total carbon, graphitic carbon, silicon, sulphur,

[1]D. W. Murphy and W. P. Wood, "Austenitic Grain Size in Cast Iron," Transactions, American Society for Metals, Vol. 24, p. 75, 1936.

[2]D. W. Murphy and W. P. Wood, "Hardenability of Cast Iron," American Foundrymen's Association, Preprint No. 37-18, 1937.

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. Of the authors, D. W. Murphy is research associate, Department of Engineering Research, W. P. Wood, professor of metallurgy, University of Michigan, Ann Arbor, Michigan, and D. Girardi, graduate student. Manuscript received June 25, 1937.

phosphorus and manganese to indicate that other factors than chemical composition, cooling rate, and graphite distribution must be operating to cause the wide fluctuations in physical properties observed. It was found in this series of irons that tensile strength and hardness in the as-cast condition increased with increasing size of a network pattern found in these irons; at the time it was suggested that this pattern might outline an austenitic grain size. The induction furnace heats in spite of similar analyses showed considerable differences in their response to hardening in that the heat showing the coarser network pattern possessed the most deep hardening characteristics.

In the second paper the authors discussed five electric furnace heats in which variations in hardening power were obtained by varying the melting practice as to amount of oxide addition and time of contact with the oxide addition and by varying the amount of aluminum used as deoxidizer. It was consistently observed in this series of heats that additions of between 0.02 and 0.03 per cent aluminum resulted in shallow hardening irons, but that the extent to which this quantity of aluminum was effective in lowering the hardenability apparently depended upon the condition of the heat with regard to oxygen prior to the aluminum addition. The physical properties showed some variation with hardenability although, since the bars were cast to 1.2 inches diameter, the variations were of lower magnitude than observed in the irons described in the first paper. The irons of shallow or low hardening power in the average case had lower tensile strength, a slightly lower transverse strength, a higher rate of deflection in the transverse test, and a higher impact strength than irons of deep or high hardening power.

As this work progressed, the results indicated that a study of austenitic grain size and rates of transformation of austenite in different types of irons, particularly the latter, would yield considerable information necessary to the understanding both of the process of hardening of cast irons and the process by which variations in grain size and hardenability affected the as-cast physical properties. This paper is concerned chiefly with the results of austenitic grain size studies and the rate of austenite transformation at 1000 degrees Fahr., by methods used in the study of these variables in steel.

In the determination of austenitic grain size two methods have been used with considerable success. The first of these consisted in heating a half cylindrical section of the as-cast bar about 3 inches

long for one hour at a temperature of 1600 degrees Fahr. At the end of this period one end was quenched in oil and the other allowed to cool in air. After rough polishing and then etching the diametral face, a section was usually revealed at which the macro grain boundaries were clearly marked out. A transverse section containing this portion of the bar was polished and etched for the purposes of grain counts.

The second method used to study the austenitic grain size was incidental to the study of rates of transformation. At some point during the transformation of austenite a condition is reached whereby the austenitic grain is defined by an outline of nodular troostite which begins to form at the austenite grain boundaries as pointed out by Bain and his associates. These methods were necessary because the irons used were completely pearlitic in nature.

The rate of transformation of austenite at 1000 degrees Fahr. was determined by quenching a series of samples (about ¼ by ⅜ by ½ inch) from 1600 degrees Fahr. into a lead-tin alloy bath maintained at 1000 degrees Fahr., holding each set of samples in the lead-tin bath for from 5 to over 200 seconds. After the proper length of time at 1000 degrees Fahr. the samples were quenched in water so that the austenite which had transformed in the time at 1000 degrees Fahr. was revealed as a dark-etching troostite while that untransformed was shown as martensite in the sample as finally cooled.

To estimate with reasonable accuracy the extent of transformation undergone in a given time at 1000 degrees Fahr., the image of a portion of the polished and etched sample at about 200 diameters was thrown on a section of translucent cross section paper giving an effect similar to that of a ground glass screen. The area of the cross section paper of approximately 3¾ inches square was divided into 3600 small squares so that the number of small squares covered by the light and dark constituents could be fairly easily determined. This process was repeated from three to five times on different sections of the same sample and the results averaged to give a reliable index of the amount of austenite transformed. The area covered by the graphite flakes was not determined since in any given section this area was counted as a part of the light or dark etching constituent.

In an earlier paper[2] the authors presented data on the hardenability of irons from five electric furnace heats which indicated that

[2]Loc. cit.

Table I
Composition, Melting Treatment and Hardenability of Five Gray Iron Heats

No.	Melting of Ladle Treatment	Tapping Temp. Degrees Fahr.	Per Cent T.C.	G.C.	C.C.	Si	Oil Quenched Hardness Rockwell C Outside	Center
A 1	None	2750	2.79	1.85	0.94	....	56	56
A 2	0.046% Al in ladle	2750	2.82	1.83	0.99	....	50	51
A 3	0.10% Al in ladle	2750	2.80	1.99	0.81	....	52	52
A 4	0.21% Al in ladle	2750	2.78	2.03	0.75	....	53	53
B 1	None	2720	2.78	1.76	1.02	1.91	56	56
B 2	0.028% Al in ladle	2720	2.78	1.85	0.93	....	54	43
B 3	0.05% Al in ladle	2720	2.76	1.92	0.84	....	54	53
B 4	0.275% Al in ladle	2720	2.78	2.00	0.78	....	54	54
C 1	None	2760	3.12	2.28	0.84	2.02	52	51
C 2	0.028% Al in ladle	2740	3.11	2.29	0.82	....	51	48
C 3	0.051% Al in ladle	2740	3.12	2.39	0.73	....	50	50
C 4	0.023% Al in furnace	2760	3.10	2.33	0.77	....	49	46
C 5	0.042% O_2 in furnace	2750	3.08	2.13	0.95	....	50	45
C 6	0.024% Al in ladle	2720	3.07	2.14	0.93	....	51	50
C 7	0.042% Al in ladle	2740	3.09	2.23	0.86	....	50	50
D 1	None	2740	3.07	2.36	0.71	1.92	54	53
D 2	0.019% Al in ladle	2740	3.09	2.30	0.79	....	51	46
D 3	0.06% Al in ladle	2750	3.10	2.20	0.90	....	51	51
D 4	0.023% Al in furnace	2760	3.08	2.29	0.79	....	50	45
D 5	0.038% O_2 in furnace	2750	3.12	2.35	0.77	....	51	44
D 6	0.015% Al in ladle	2750	3.09	2.29	0.80	....	50	43
D 7	0.041% Al in ladle	2740	3.08	2.16	0.92	....	51	50
E 1	None	2730	2.97	2.16	0.81	2.00	54	54
E 2	0.019% Al in ladle	2720	2.97	1.91	1.06	....	52	45
E 3	0.041% O_2 in furnace[1]	2700	2.99	2.07	0.92	....	53	52
E 4	0.041% O_2 in furnace	2700	2.97	2.19	0.78	....	56	55
E 5	0.017% Al in ladle	2700	2.97	2.08	0.89	....	51	42
E 6	0.041% O_2 in furnace	2680	2.97	2.22	0.75	....	55	55
E 7	0.018% Al in ladle	2650	2.97	2.11	0.86	....	50	41
E 8	0.024% Al in furnace[2]	2680	2.95	2.18	0.77	....	53	47
E 9	0.024% Al in furnace	2650	2.94	2.12	0.82	....	54	51
E 10	0.024% Al in furnace	2600	2.87	2.02	0.85	....	55	54

[1]Oxygen added as ferric oxide after tapping E2, E3, E4, E6 tapped 4 min. 5 sec., 6 min. 27 sec., and 10 min. 35 sec. after oxide addition. E5 and E7 tapped 8 min. 28 sec., and 12 min. 55 sec. after oxide addition.

[2]Alum. added 14 min. 45 sec. after oxide addition. E8, E9, E10 tapped 15 min. 30 sec., 20 min. 1 sec. and 25 min. 8 sec. after oxide addition.

0.02 to 0.03 per cent of aluminum added to the ladle was very effective in reducing hardening power. Table I summarizes the outside and center hardness of oil quenched portions of the standard 1.2 inch diameter arbitration bars, the chemical composition and the melting treatment.

Microscopic examination of the samples used for hardenability measurements in the deep and shallow hardening irons showed some consistent differences in hardened structures. The deep hardening types invariably quenched to a full martensitic structure in a 1.2-inch diameter bar while the shallow hardening irons invariably had a considerable amount of the constituent formed by the high temperature acicular mode of austenite transformation[3] as well as some nodular troostite. Examples of the most frequent types of hardened

[3]J. R. Vilella, G. E. Guellich and E. C. Bain, "On Naming Aggregate Constituents," TRANSACTIONS, American Society for Metals, Vol. 24, p. 225, 1936.

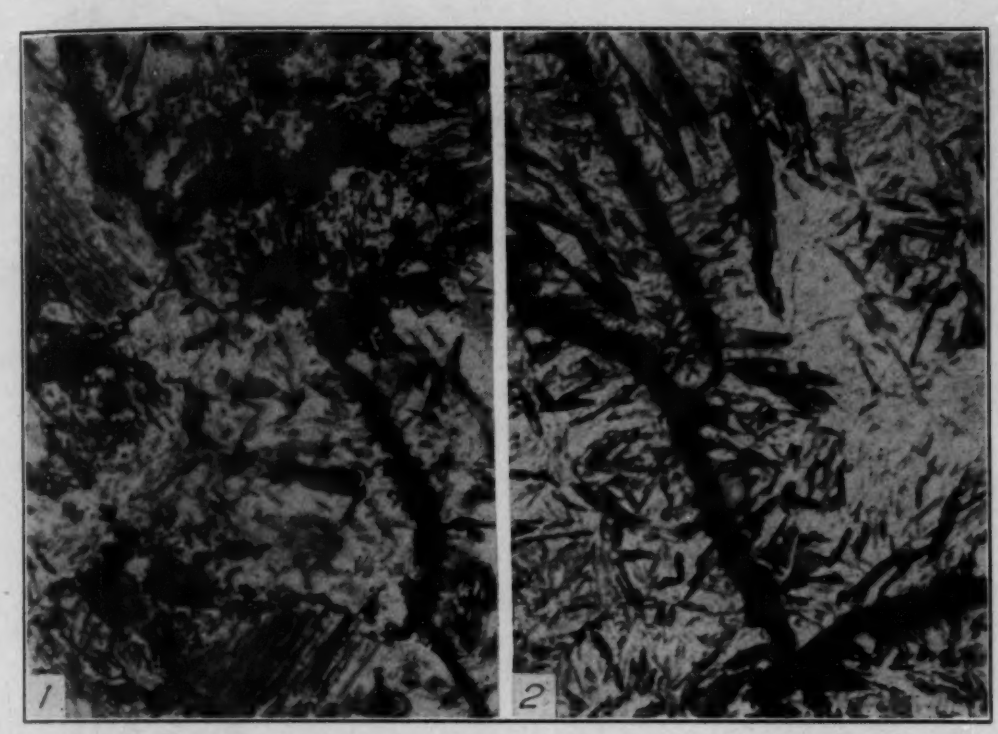


Fig. 1—Structure of Hardenability Sample from E7. Oil Quenched from 1525 Degrees Fahr. Etched with 4 Per Cent Nital. × 1000.
Fig. 2—Structure of Hardenability Sample from E4. Oil Quenched from 1525 Degrees Fahr. Etched with 4 Per Cent Nital. × 1000.

structures in the shallow and deep hardening irons are given in Figs. 1 and 2 which are photomicrographs of irons E7 and E4, respectively. In Fig. 3 the hardness penetration data for bars of these two irons quenched from 1525 degrees Fahr. is summarized. Notwithstanding small differences in combined carbon (Table I) E4 is intensely deep hardening while E7 was the most shallow hardening iron produced in any of the heats. Considering the characteristic differences in the hardened structures it appeared as though large differences in the rate of austenite transformation at subcritical temperatures must exist between these two types of irons in the direction of decreasing rate of transformation with increasing hardening power.

In order to arrive at a more thorough understanding of the hardening process in gray cast iron it was apparent that a more accurate knowledge of the rates of austenite transformation would be of considerable importance in explaining the present case and in addition would furnish a reasonable basis for comparison with similar research in steel. Because of the wide variation in hardening power previously observed in irons E4 and E7 these were chosen for this portion of the investigation which has been limited for the

present to a study of the transformation rates of austenite at 1000 degrees Fahr.

Both irons in the as-cast condition, Figs. 4 and 5, were entirely pearlitic with some slight formation of carbide. Graphite in both cases was present for the most part in a random arrangement, although there was a slight tendency toward the formation of den-

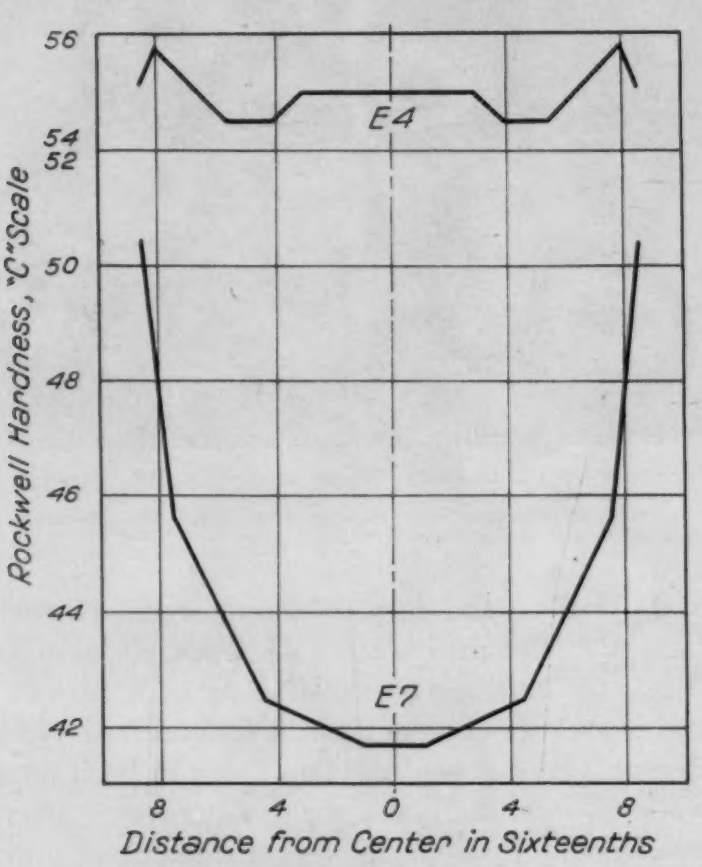


Fig. 3—Hardenability of Samples E4 and E7. Oil Quenched from 1525 Degrees Fahr.
E4—Tapped 6 Minutes 27 Seconds after Addition of Oxide.
E7—0.018 Per Cent Aluminum in Ladle. Tapped 12 Minutes 55 Seconds After Addition of Oxide.

dritic graphite patterns, particularly toward the outside of the bars E4. The large grain size as developed by the first method previously described is shown in Figs. 6 and 7, while that which appeared clearly near the end of the transformation period is shown in Figs. 8 and 9. Both methods evidently developed the same structural network, E4 showing the coarsest pattern and E7 the finest. It will be recalled that in Fig. 3, E4 was characterized by deep hardening qualities and E7 by shallow hardenability. This observation con-

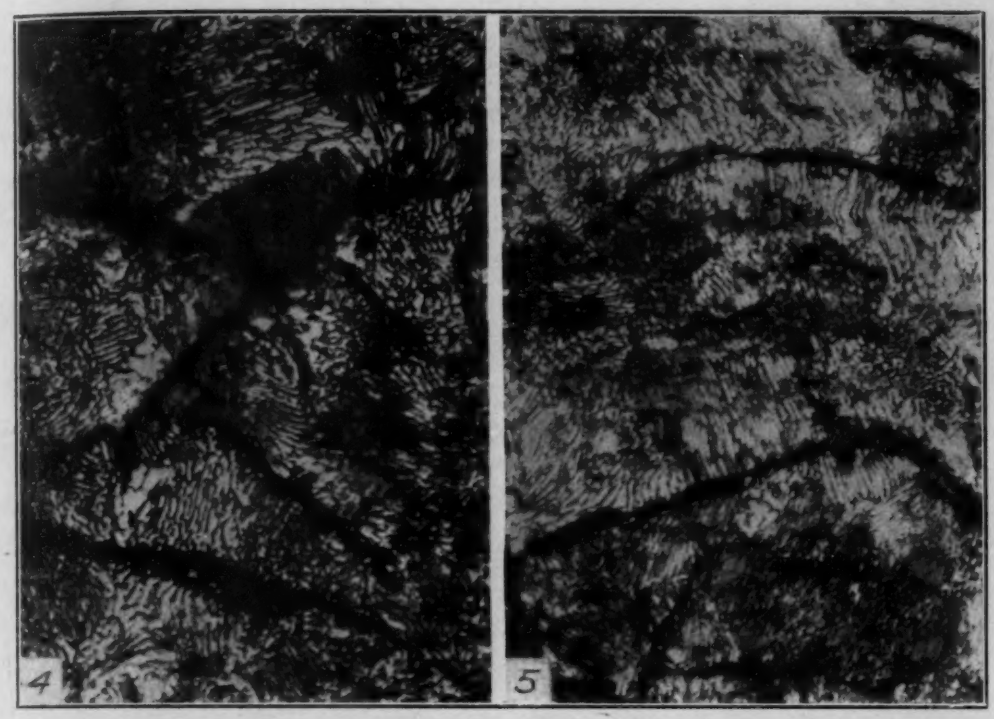
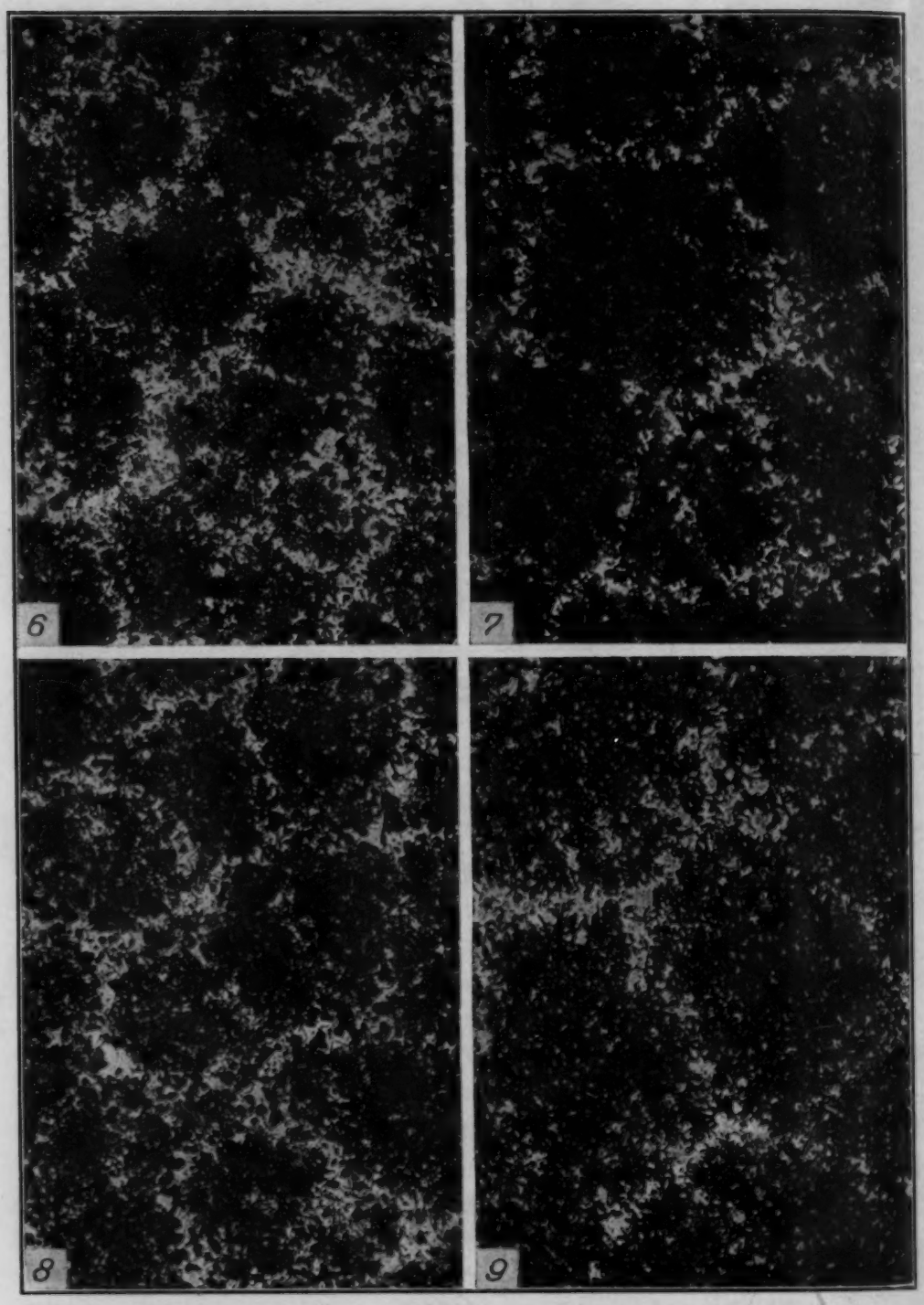


Fig. 4—Structure of E7 as Cast. Etched with 4 Per Cent Nital. × 1000.
Fig. 5—Structure of E4 as Cast. Etched with 4 Per Cent Nital. × 1000.

firms a finding reported in the first paper[1] in this series in that the irons showing the coarsest network tended to show the greatest hardenability.

The progress of the austenite transformation in both coarse- and fine-grained samples is illustrated in Figs. 10 through 17. A holding period of 30 seconds at 1000 degrees Fahr. produced the condition in E7 shown in Fig. 10, while a period of 60 seconds in the case of E4 (Fig. 11) was insufficient to attain the same extent of transformation. Furthermore, as in the case of steel, the product of austenite transformation at 1000 degrees Fahr. is nodular troostite. Figs. 12 and 13 show the condition of E7 and E4 after 45 and 75 seconds respectively; the breakdown has progressed in each case but E4 lags considerably behind E7. Comparing the samples held for 75 seconds in the case of E7 and 120 seconds in the case of E4 (Figs. 14 and 15) it will be seen that both have undergone approximately the same degree of transformation. In the last two figures of this series, 16 and 17, both samples having been held for 150 seconds at 1000 degrees Fahr., the fine-grained iron E7 shows practically complete transformation, while the coarse-grained iron E4 is still incomplete, although closer in condition to that of E7 than in the previous figures.



Macro Grain Size as Developed by Differential Quench Method.
Fig. 6—Macro Grain Size of Iron E7. Etched with 4 Per Cent Nital. × 30.
Fig. 7—Macro Grain Size of Iron E4. Etched with 4 Per Cent Nital. × 30.
Fig. 8—Macro Grain Size of Iron E7. Etched with 4 Per Cent Nital. Held 75 Seconds at 1000 Degrees Fahr. × 30.
Fig. 9—Macro Grain Size of Iron E4. Etched with 4 Per Cent Nital. Held 120 Seconds at 1000 Degrees Fahr. × 30.

Data on all of the samples used in this investigation are summarized in the curves of Fig. 18 in which the amount of austenite decomposed is plotted against time of holding at 1000 degrees Fahr. The reaction begins in the fine-grained iron, E7, with a holding period of between 5 and 10 seconds at 1000 degrees Fahr. while in the coarse-grained iron, E4, the reaction is not initiated until about 35 or 40 seconds have elapsed. As far as the body of the large grains is concerned (Figs. 6, 7, 8 and 9) it requires about 130 to 140 seconds for completion of the reaction after it once begins, regardless of the grain size. The great difference between the deep and shallow hardening irons is very evidently the length of time required to initiate the reaction of the decomposition of austenite which is much shorter in fine-grained irons than in the coarse-grained types. This explains the vast difference in the structures of the oil hardened samples shown in Figs. 1 and 2; in the case of E4 the cooling rate produced by the oil was sufficient to bring the temperature of the sample to that required for the formation of martensite before the high temperature reactions could begin, while in the case of E7 the cooling rate was so slow as to prevent only partially the high temperature austenite reactions. It might be pointed out here that compared to the austenite decomposition at 1000 degrees Fahr. in carbon steel the reactions in cast iron are much slower to start and much slower in progressing to completion.

In carrying out the studies on rates of transformation additional information on grain size was developed which permits some speculation with regard to the nature of the network previously developed. It became apparent that the transformation of austenite was not beginning at this coarse network but rather at a finer network as shown in Figs. 19 and 20 which show the conditions in E7 and E4 during the early stages of decomposition. The network here developed is one of nodular troostite surrounding an austenite-martensite matrix. Theories regarding the transformation of austenite quite uniformly require that the reaction for the most part be initiated at the austenite grain boundary. It appears therefore as though the austenite grain size effective on reheating is this finer network shown in Figs. 19 and 20. The graphite flakes will most frequently be found in the boundary as outlined by the nodular troostite. Two facts should be pointed out here with regard to the graphite flakes. First, one flake may serve as a common boundary for several austenite grains as defined by the nodular troostite, and second, the

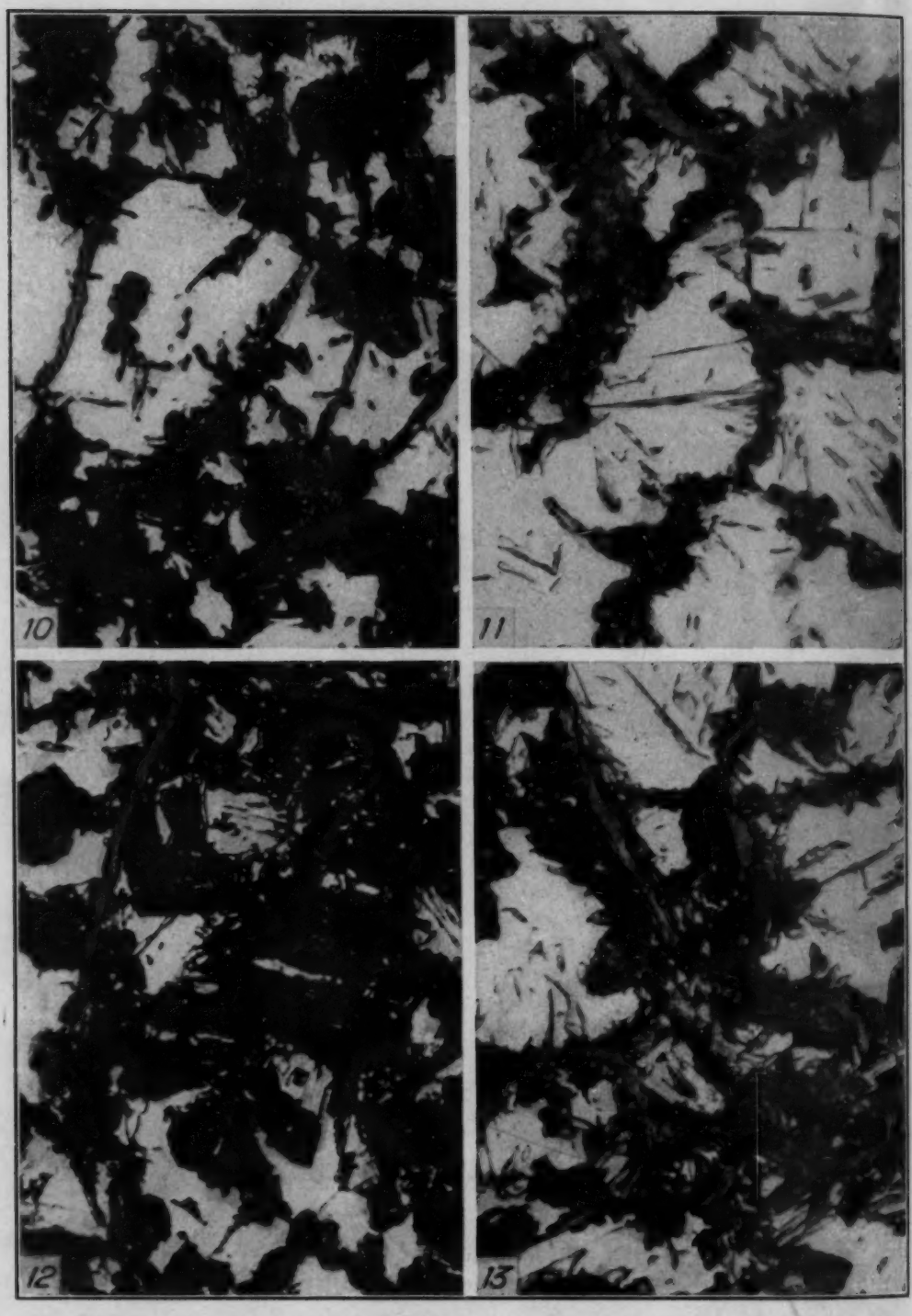


Fig. 10—Structure of Iron E7 After 1 Hour at 1600 Degrees Fahr., 30 Seconds at 1000 Degrees Fahr. and Water Quenching. Etched with 4 Per Cent Nital. × 1000.
Fig. 11—Structure of Iron E4 After 1 Hour at 1600 Degrees Fahr., 60 Seconds at 1000 Degrees Fahr. and Water Quenching. Etched with 4 Per Cent Nital. × 1000.
Fig. 12—Structure of Iron E7 After 1 Hour at 1600 Degrees Fahr., 45 Seconds at 1000 Degrees Fahr. and Water Quenching. Etched with 4 Per Cent Nital. × 1000.
Fig. 13—Structure of Iron E4 After 1 Hour at 1600 Degrees Fahr., 75 Seconds at 1000 Degrees Fahr. and Water Quenching. Etched with 4 Per Cent Nital. × 1000.

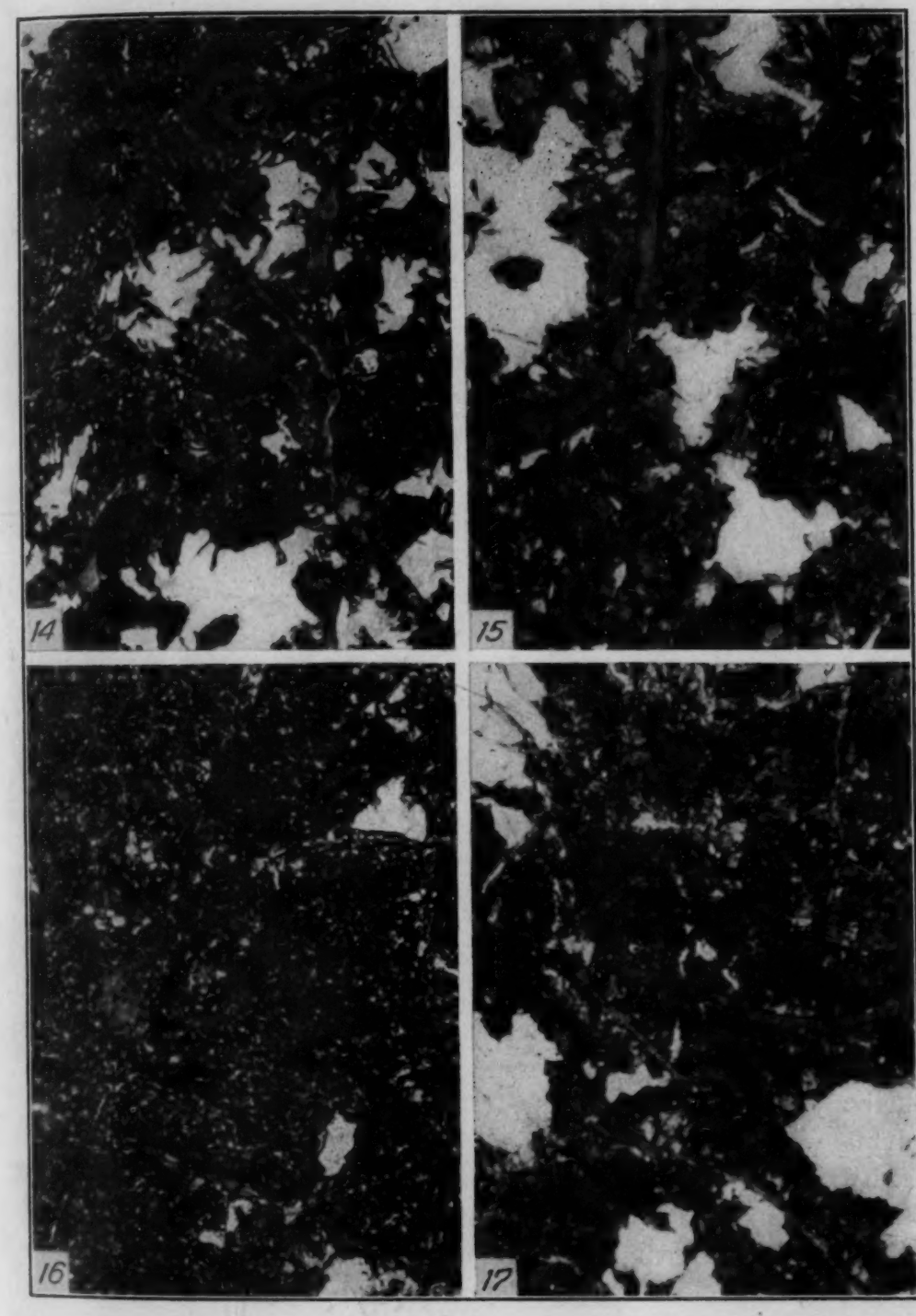


Fig. 14—Structure of Iron E7 After 1 Hour at 1600 Degrees Fahr., 75 Seconds at 1000 Degrees Fahr. and Water Quenching. Etched with 4 Per Cent Nital. × 1000.
Fig. 15—Structure of Iron E4 After 1 Hour at 1600 Degrees Fahr., 120 Seconds at 1000 Degrees Fahr. and Water Quenching. Etched with 4 Per Cent Nital. × 1000.
Fig. 16—Structure of Iron E7 After 1 Hour at 1600 Degrees Fahr., 150 Seconds at 1000 Degrees Fahr. and Water Quenching. Etched with 4 Per Cent Nital. × 1000.
Fig. 17—Structure of Iron E4 After 1 Hour at 1600 Degrees Fahr., 150 Seconds at 1000 Degrees Fahr. and Water Quenching. Etched with 4 Per Cent Nital. × 1000.

outline of a grain is normally completed independently of the graphite. In this sense the flakes seem to have some of the characteristics of inclusions.

The coarse network as shown in Figs. 6, 7, 8 and 9 was observed to have a much slower rate of transformation than the body of the grain, so much so that when the body of one of these large grains showed complete transformation a considerable increase in time of holding at 1000 degrees Fahr. was necessary to appreciably increase the

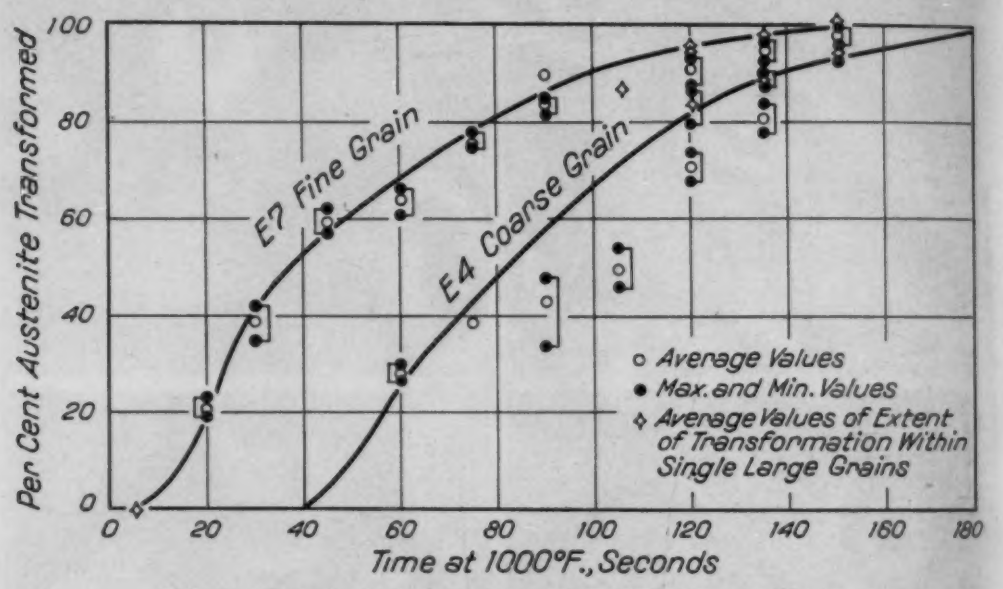


Fig. 18—Transformation of Austenite at 1000 Degrees Fahr.

boundary decomposition. In an attempt to arrive at a reasonable explanation, a sample of the E7 series which had been held for 90 seconds at 1000 degrees Fahr. and showed between 80 and 90 per cent of the austenite transformed was etched with alkaline sodium picrate. As expected, this sample showed a marked carbide precipitation in the body of the grain and none at all in the boundary (Fig. 21). This sample was then given a 10-minute draw at 1000 degrees Fahr. in the lead bath and repolished and etched in sodium picrate with the result shown in Fig. 22. The body of the grain quite naturally had not been affected by the 10-minute draw but the boundary material as shown by the lighter colored area had precipitated free carbide in sufficient quantity to decidedly alter the original appearance but insufficient to cause the same degree of darkening on etching. It seems reasonable to infer from this that the boundary material as revealed by methods previously described is in reality a region of low carbon content although there may be other differences in composition between this

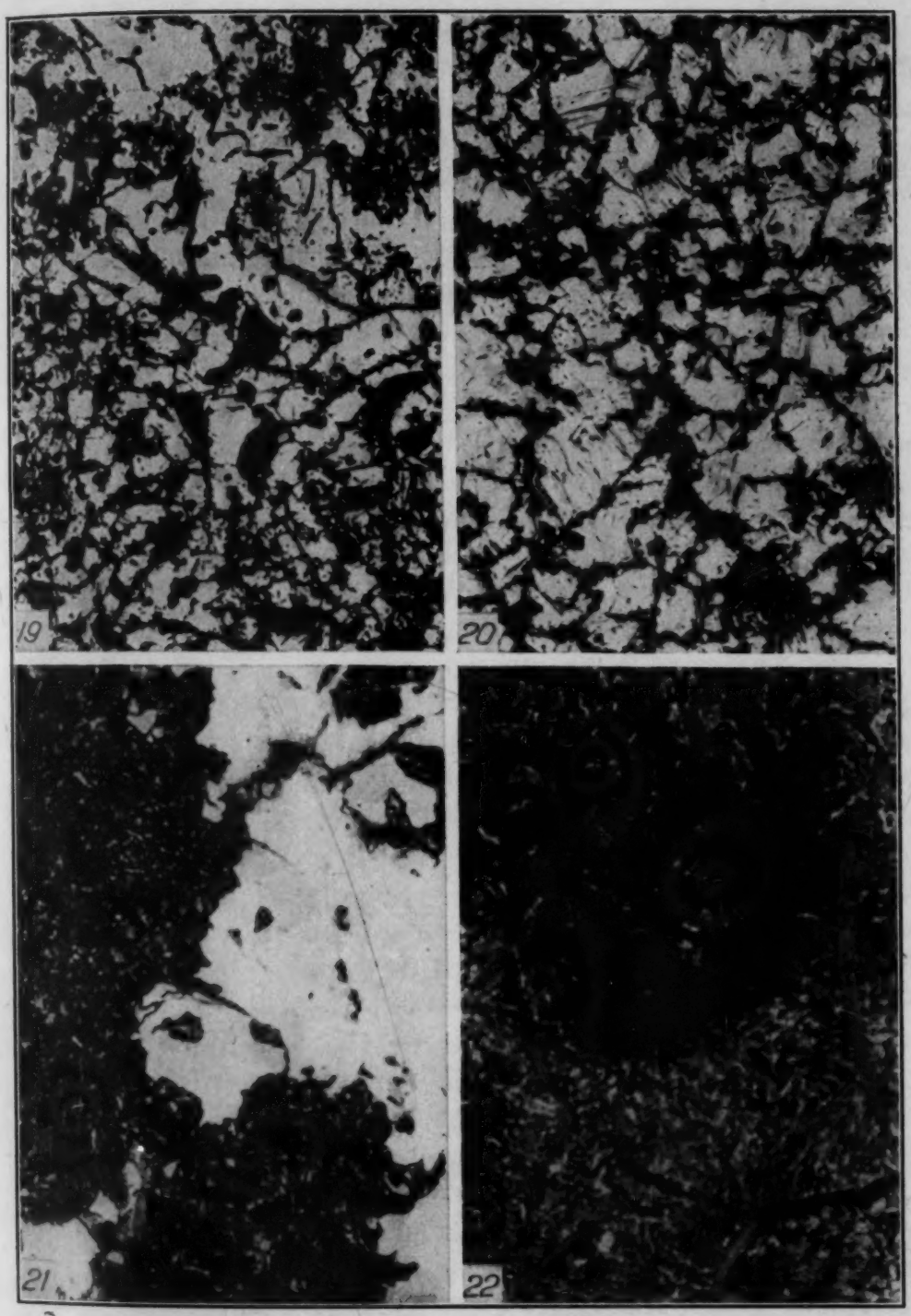


Fig. 19—Structure of Iron E7 After 1 Hour at 1600 Degrees Fahr., 30 Seconds at 1000 Degrees Fahr. and Water Quenching, Showing Fine Network Outlined by Nodular Troostite. Etched with 4 Per Cent Nital. × 200.

Fig. 20—Structure of Iron E4 After 1 Hour at 1600 Degrees Fahr., 75 Seconds at 1000 Degrees Fahr. and Water Quenching, Showing Fine Network Structure Outlined by Nodular Troostite. Etched with 4 Per Cent Nital. × 200.

Fig. 21—Structure of Iron E7 After 1 Hour at 1600 Degrees Fahr., 90 Seconds at 1000 Degrees Fahr. and Water Quenching. Etched in Boiling Sodium Picrate to Show Free Carbide. × 1000.

Fig. 22—Same Sample as in Fig. 21 Except Given 10 Minute Draw at 1000 Degrees Fahr. to Precipitate and Carbide in Grain Boundary. Etched with Boiling Sodium Picrate. × 1000.

coarse boundary and the body of the grain. From the fact that these irons contained only about 0.04 to 0.06 per cent phosphorus it seems as though phosphorus is not essential to establish this network, although it may be admitted that 0.2 to 0.4 per cent would probably aid in its resolution, perhaps even without heat treatment. What other possible segregations may contribute to the formation and permanence of this network it is difficult to say.

It seems evident now that the coarse network developed or accentuated by the methods given here is the trace of a condition which existed in the iron after solidification, but while it was yet at a very high temperature. At this point in the history of the casting it seems probable that a certain amount of segregation to the existing austenite boundaries occurs so that the network either shows fairly well in the as-cast condition or can be accentuated by a proper heat treatment. The evidence for segregation is rather indirect, but some differences in carbon solubility must exist at these boundaries as compared with the body of the grain in view of the considerable difference in their reaction to sodium picrate. The location of these coarse boundaries is seemingly independent of the graphite flakes as well as the dendritic solidification pattern. Graphite flakes are easily found in the grain boundaries and frequently one dendrite may be traced in several of the grains marked out by the coarse network or one grain may contain portions of several dendrites. Additional evidence supporting this view of the origin of this network is the fact that except in quite small sections the apparent size of the network increases from outside toward the center.

The fine grain pattern developed in the early stages of austenite transformation at 1000 degrees Fahr. seems to be the effective austenite grain size at least on reheating to the austenitic state. This grain structure is likewise independent of the dendritic solidification pattern and although graphite flakes may lie in or serve as grain boundaries with similar graphite arrangement a wide variation in size of grains is possible. Contrary to the variation of the coarse network from outside to center the fine network pattern has a fairly constant size from outside to the center of the casting. Although the relative sizes of the fine network structures in these irons paralleled the relative sizes of the coarse network structures there is scarcely sufficient evidence to say that this behavior will always be followed..

In conclusion, a brief summary of the salient points developed in this investigation may be offered:

(1) Deep and shallow hardening irons are characterized by vastly different structures in the hardened condition using the normal practice of oil quenching.

(2) The origin of these different hardened structures is found in the very different rates of austenite transformation at subcritical temperatures.

(3) At 1000 degrees Fahr. the deep hardening irons are very sluggish to transform from austenite, the reaction producing nodular troostite requiring about 35 to 40 seconds to be initiated and approximately 130 to 140 seconds after once starting to go to completion, except for the area involved in the coarse macro network.

(4) At 1000 degrees Fahr. the shallow hardening irons are much less sluggish to transform from austenite, this reaction requiring in this case between 5 and 10 seconds for initiation and again about 130 to 140 seconds after starting for completion.

(5) The coarse macro network was found to be very persistent and very much slower than the matrix in its transformation. There appears to be a carbon deficiency in the areas comprising these boundaries which quite possibly results from some segregation at very high temperatures.

(6) The present data indicate that this coarse pattern is a trace of an austenitic grain size developed in the casting while just below the point of final solidification.

(7) A very fine network structure can be developed in irons during the early stages of austenite decomposition at 1000 degrees Fahr. in which the pattern is outlined by the formation of dark etching nodular troostite with a matrix of light etching austenite-martensite.

(8) This fine network structure is probably representative of the effective austenitic grain size on reheating.

(9) Deep hardening irons so far investigated are found to have a coarse macro and micro network structure while the shallow hardening irons have a fine macro and micro network structure.

(10) Compared to the time required in steels for initiation of austenitic decomposition and completion of this decomposition at 1000 degrees Fahr., the reactions in gray cast irons are much more sluggish.

ACKNOWLEDGMENT

The authors desire to express their deep appreciation to Professors A. E. White and C. W. Good of the Department of Engineering Research and Professor A. H. White of the Department of Chemical and Metallurgical Engineering for their continued interest in this problem and for their aid in securing the financial support necessary to carry it forward.

DISCUSSION

Written Discussion: By A. I. Krynitsky, associate metallurgist, National Bureau of Standards, Washington, D. C.

The authors are to be commended for introducing this subject at this time and for their study of this very complicated problem involving a great number of observations.

It is logical to believe that the cast iron matrix should have similar properties to that of steel.

Whatever is the nature of the network structure shown on their macrographs (Figs. 6, 7, 8 and 9) the data presented seem to indicate that there is a correlation between the size of these cells and the depth of hardening of the irons examined quite similar to the hardenability-austenitic grain size relation existing in steel. However, the following remarks may be of some interest.

The correlation mentioned above has been observed in all irons but iron B2 from the authors' second paper. This iron was treated with 0.028 per cent of aluminum added in the ladle and was shown to be a shallow hardening iron. Yet it exhibited very coarse-grained characteristics. No explanation for this inconsistency has been offered by the authors. Assuming that we are dealing here with a true austenitic grain structure, reference then can be made to an observation of McQuaid[1] that a certain heat of steel, in spite of the large increase in grain size, showed very little increased hardenability as compared with another heat, due primarily to the fact that a considerable portion of the carbide was not yet in solution.

The results obtained with irons C6 and D6 are of particular interest. From the previous paper[2] it seems that the melting conditions and treatment of these melts were about the same. However, iron C6 was found to be a deep hardening iron while iron D6 was a shallow hardening one. It is rather doubtful whether such a pronounced difference can be explained by a difference (0.009 per cent) in the total amount of aluminum added to the melt or by a difference in the combined carbon and silicon contents in these irons. It is evident, however, that an addition of practically the same amount of aluminum had quite a different effect on both melts. It may be assumed that the aluminum which is added to

[1]H. W. McQuaid, "A Study of the Effect of the Aluminum Addition on the Structure of a Quenched Carbon Steel," TRANSACTIONS, American Society for Metals, Vol. 25, No. 2, June 1937, pages 490-519.

[2]D. W. Murphy and W. P. Wood, "Hardenability of Cast Iron," American Foundrymen's Association. Preprint No. 37-18, 1937.

the molten iron is partly removed from it during skimming, partly dispersed as Al_2O_3 inclusions throughout the melt, and partly forms a solid solution with iron. Very interesting information on some factors influencing austenitic grain size in high purity steels is presented by Derge, Kommel and Mehl[3].

The results obtained led them to the conclusion that "Al_2O_3 and SiO_2 inhibit grain growth; whereas aluminum and silicon in solid solution do not, and that the degree of inhibition is closely related to the type of dispersion of the oxides."

This conclusion can probably be used as an argument explaining the observed difference.

It would be of great interest to learn whether titanium-carbon dioxide modification treatment of the molten iron produces any effect on its hardening property.

One can find an indication in the previous paper[2] and in Fig. 20 of this paper that the graphite flakes are arranged along the grain boundaries.

With regard to the nature of the network previously developed the authors state that "it became apparent that the transformation of austenite was not beginning at this coarse network but rather at a finer network as shown in Figs. 19 and 20." It appears to them therefore "as though the austenite grain size effective on reheating is this finer network." In other words, as the writer understands it, the large grains of austenite on reheating consist here of a number of small austenite grains which are the main factors in the transformation of austenite. The authors observed that the graphite flakes are most frequently found in the boundary of these small grains as outlined by the nodular troostite, which fact leads them to believe that first, graphite flakes may serve as a common boundary for several austenite grains and second, the outline of a grain is normally completed independently of the graphite, and flakes have some of the characteristics of inclusions.

A further speculation in this direction may lead us to the hypothesis that the transformation of austenite was stimulated here by the presence of graphite network. If this is really so then a knowledge of the unetched structure of the irons examined is of prime importance.

From their experiments with the etching in boiling sodium picrate (Figs. 21 and 22) the authors infer that "the boundary material of the coarse network is in reality a region of low carbon content although there may be other differences in composition between this coarse boundary and the body of the grain." Without attempting to discuss the nature of this coarse network, the writer wants only to note that it was observed by McQuaid[1] that "the presence of the ferrite envelopes indicates that either diffusion of the carbon had not been sufficient to completely obliterate the grain boundary ferrite or that the solubility of the carbon in the grain boundary ferrite itself had been greatly decreased as compared to the remainder of the grain." He found that "where the carbon had diffused to the grain boundaries that the final result had been a complete elimination of the grain boundary ferrite and the resulting merging of two grains of austenite into one."

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[3]G. Derge, A. R. Kommel and R. F. Mehl, "Some Factors Influencing Austenitic Grain Size in High Purity Steels," which is published in this issue of TRANSACTIONS beginning on page 153.

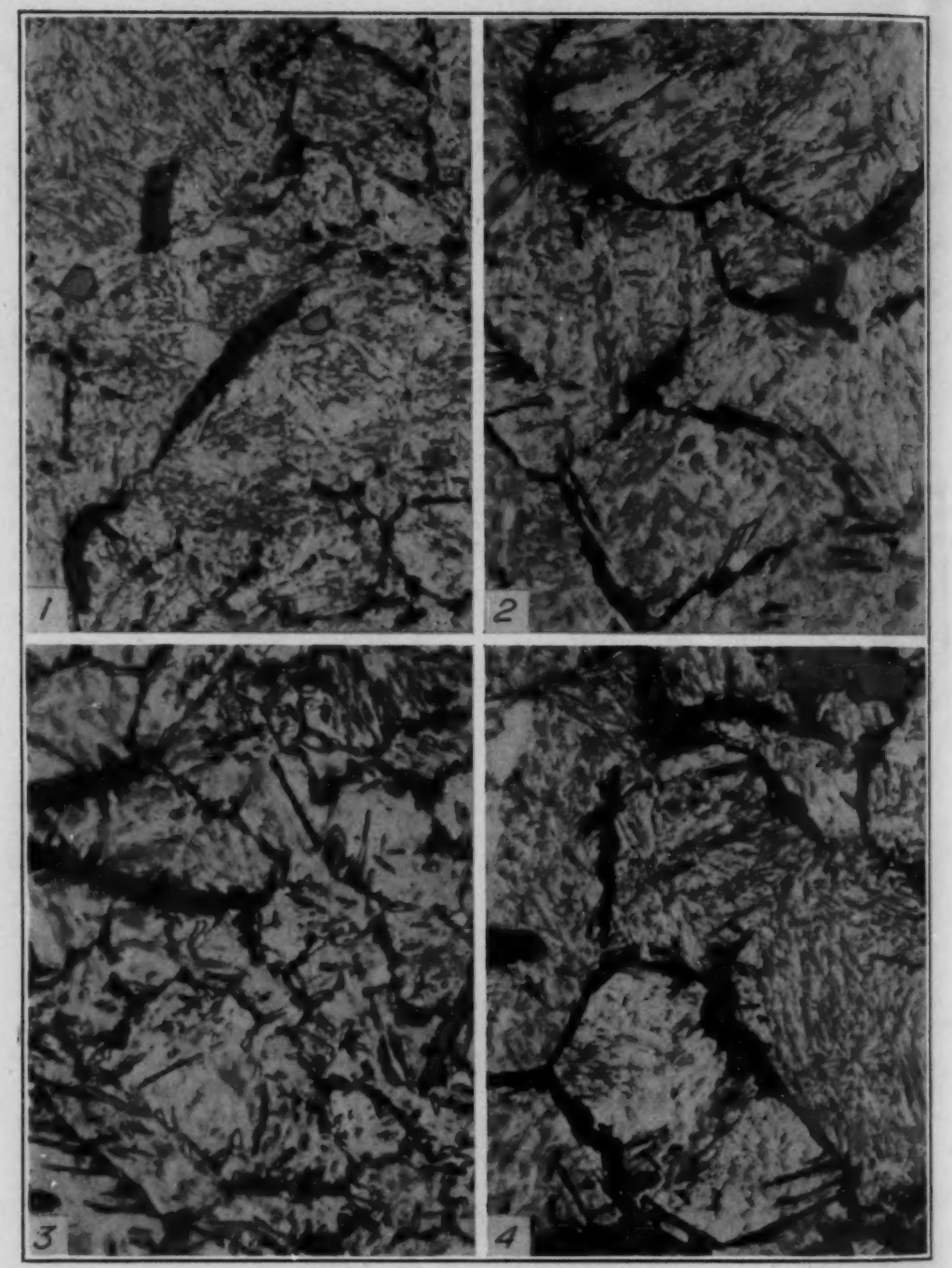


Fig. 1—Iron E7 after 1 Hour at 1600 Degrees Fahr., 10 Seconds at 1000 Degrees Fahr. and Water Quenching.

Fig. 2—Iron E4 after 1 Hour at 1600 Degrees Fahr., 30 Seconds at 1000 Degrees Fahr. and Water Quenching.

Fig. 3—Iron E7 after 1 Hour at 1600 Degrees Fahr., 20 Seconds at 1000 Degrees Fahr. and Water Quenching.

Fig. 4—Iron E4 after 1 Hour at 1600 Degrees Fahr., 45 Seconds at 1000 Degrees Fahr. and Water Quenching.

All Specimens Etched with 4 Per Cent Nital. × 1000.

Authors' Closure

The authors appreciate the discussion offered by Mr. Krynitzky since it calls attention to some of the points which were perhaps too little emphasized in the paper. We would like to discuss first the question of whether the graphite distribution plays an important role in initiating the austenite transformation. Figs. 1, 2, 3 and 4 of this closure may shed considerable light on this problem. In the first two photomicrographs showing the very beginning of transformation it will be seen that the austenite begins to transform at grain boundaries not associated with graphite flakes at all; in other words the transformation begins in the austenitic matrix of the iron between the flakes. Figs. 3 and 4 show that when the transformation has progressed to a greater extent the graphite flakes will be found in the austenitic grain boundaries. Apparently, then, the transformation begins without regard to the graphite distribution but since the flakes usually are found in the grain boundaries after further transformation it is entirely possible that the graphite distribution may limit the extent to which these fine austenite grains might grow on heating to temperatures in the austenite field.

It is quite possible as pointed out by Mr. Krynitzky that in the case of iron B2 which showed a coarse grain size and shallow hardenability that all of the carbide was not in solution at the time of quenching. As pointed out by McQuaid this condition would lead to shallow hardenability.

The authors are in agreement with Mr. Krynitzky's observations with regard to the occasional dissimilarity of results obtained from given aluminum additions. All of the work done to date indicates that the dispersion of oxides or condition of oxidation of the heat prior to the addition of aluminum is fully as important as the amount of aluminum added in determining the subsequent grain size and hardenability characteristics of the solid iron.

Mr. Krynitzky apparently agrees with the authors that the coarse macro grain boundaries observed in these studies are regions of lower carbon concentration than the body of the grain. It cannot be stated in the light of our present knowledge what causes the difference in carbon concentration, but the fact remains that it is an extremely persistent structural condition which so far we have not been able to completely obliterate.

THE FATIGUE RESISTANCE OF STEEL AS AFFECTED BY SOME CLEANING METHODS

By J. H. Frye, Jr., and G. L. Kehl

Abstract

An investigation was made to determine the effect of some descaling methods on the endurance limit of steel. Particular attention was paid to scale removal by sand, steel shot, and steel grit blasting. A correlation was made between the surface and the fatigue limits. The relation between angle of blasting with sand dust and blasting pressure is shown. Complete fatigue curves are presented together with corresponding photomicrographs of the blasting medium used and the resulting notch development.

Introduction

IT is usually necessary prior to the metallic coating of steel either by hot dipping methods or electroplating to remove thoroughly all oxide scale from the surface of the steel to insure an adherent coating. Descaling methods are also frequently employed for a natural finish. In these cleaning operations not only is scale and surface dirt removed, but the surface of the steel may also be altered. It is recognized that this alteration of the surface may considerably affect the fatigue resistance of the steel either in the cleaned or in the cleaned and plated condition. Thus it is seen that cleaning of material subject to vibrating stresses is important not only as a means of surface conditioning, but also in its effect on the endurance limit. The investigation of surface preparation of metals in progress at Lehigh University is being devoted to the problem of securing good cleaning and plating conditions together with the least detrimental effect on the endurance strength of the cleaned or cleaned and plated material. This paper is a report of the work done on cleaning by sand, steel grit, and steel shot blasting in relation to the endurance limit.

The material here presented is from a thesis submitted by G. L. Kehl in partial fulfillment for the degree of Master of Science at Lehigh University.

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. Of the authors, J. H. Frye is Instructor and G. L. Kehl is Metallurgical Research Fellow, Department of Metallurgy, Lehigh University, Bethlehem, Pa. Manuscript received June 25, 1937.

The factors affecting the fatigue limit of steel are sufficiently well understood to permit their use as a guide in this investigation. Two fundamentals already reported by many investigators are that notches on the surface of steel will decrease and that cold work will increase the endurance limit. It would seem reasonable to suspect that any deformation of the surface of steel might also increase the fatigue limit and this fact has recently been proven. Horger[1] obtained surface deformation of steel by cold rolling and Weibel[2] by shot blasting polished specimens of Swedish spring steel. In each case an increase in fatigue limit was obtained.

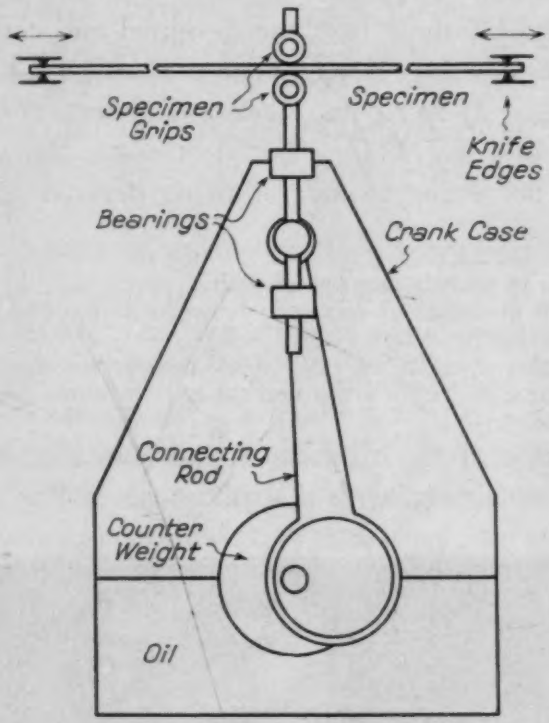


Fig. 1—Schematic Diagram of Fatigue Machine.

It would seem advisable to consider at this point the possible effect of the two common cleaning methods, pickling and blasting, on the fatigue strength of steel as usually measured by subjecting a highly polished specimen to alternating stresses. Acid pickling will produce surface pitting of steel which may, of course, be restricted somewhat by the addition of inhibitors. However, it would appear that with perfect conditions of pickling the fatigue strength of the

[1]O. J. Horger, "Effect of Surface Rolling on the Fatigue Strength of Steel," *Transactions*, American Society of Mechanical Engineers, 1935, p. 128.

[2]E. E. Weibel, "The Correlation of Spring-Wire Bending and Torsion Fatigue Tests," *Transactions*, American Society of Mechanical Engineers, 1935, p. 501.

pickled steel could only approach that of the polished specimen as a limit.

Blasting, on the other hand, produces two surface effects, notches and cold work. The first is deleterious, the second beneficial within limits. If means can be found of mitigating the former and intensifying the latter, then the possibility of raising the fatigue limit is apparent.

Apparatus And Procedure

Fatigue Machine—The investigation was carried out on a reversed bending type fatigue machine designed and constructed in the Metallurgical Engineering Department of Lehigh University; it operated at a speed of 1750 r.p.m. Constant deflection of the specimen was maintained and, to obtain desired stresses, the specimens were varied in length according to the following derived formula:

$$sl^2 = 12\Delta Ec$$

where s = stress in pounds per square inch
l = length in inches of specimen between knife edge grips
Δ = deflection in inches (0.375 inch)
E = modulus of elasticity (29,400,000 pounds per square inch)
c = distance in inches from neutral axis to outer fibers (0.0625 inch)

A cross section of the machine is shown in Fig. 1 and the action of the specimen as viewed with a stroboscope in Fig. 2.

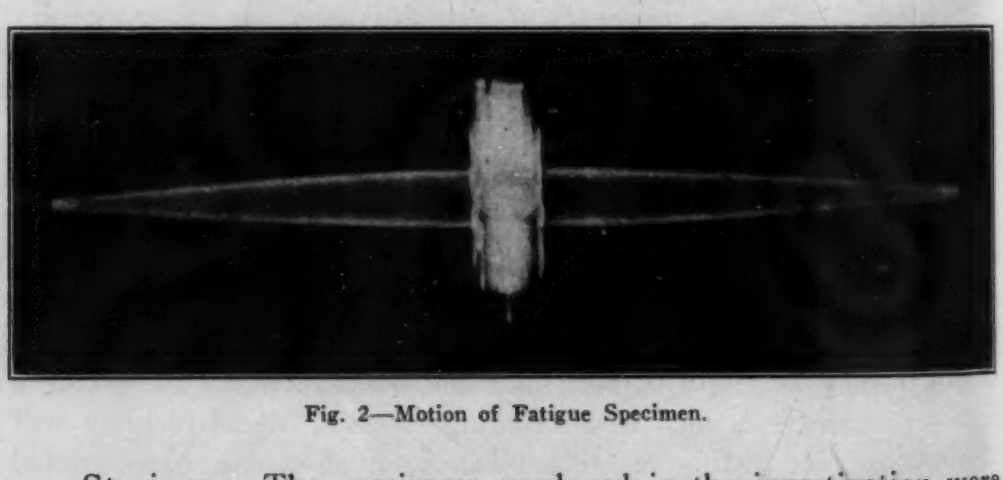


Fig. 2—Motion of Fatigue Specimen.

Specimens—The specimens employed in the investigation were contributed by John A. Roebling's Sons Co. The specimens were cold-rolled from a heat treated round wire rod to ⅛ inch x ½ inch cross section. The flat wire was continuously heat treated at 1650 degrees Fahr. (900 degrees Cent.) and quenched in molten lead

at a temperature of 900 degrees Fahr. (480 degrees Cent.). This final heat treatment produced a fine pearlitic (sorbitic) structure.

The wire was then passed through cold rolls to effect any straightening that might be necessary, and finally cut into 24-inch lengths. Actual specimen test lengths varied from 10.95 to 15.00 inches.

To determine whether or not the straightening operation had produced any surface cold working, Vickers hardness measurements were made on rouge-polished specimens with various major testing loads. By using several major testing loads, the hardness could be determined at various distances from the surface. From the Vickers hardness number, the depth of penetration of the diamond pyramid could be determined.

It was found that the hardness readings were in very close agreement to a depth of 0.00372 inch, excepting those readings to a depth of 0.000779 inch.

Lead spots picked up during the heat treatment of the steel were plainly visible on the surface being tested and it is thought that the low readings obtained near the surface were due to these spots. It was possible, however, that decarburization might be a contributory cause and since decarburization would lower the fatigue limit of steel, a microscopic examination was made to determine if any were present. To protect the edges, a specimen was electroplated with zinc in a neutral zinc solution, mounted in a steel ring for polishing, and examined at 1000 diameters. No decarburization was discernible.

The chemical composition and physical properties of the material are shown below:

Chemical composition, per cent: C, 0.541; Mn, 0.600; P, 0.026; S, 0.024; Si, 0.198.

Physical Properties*

Ultimate Strength	115,700 Pounds Per Square Inch
Yield Point	76,700 Pounds Per Square Inch
Per Cent Elongation in 2 Inches	14.5 Per Cent
Reduction in Area	40.0 Per Cent
Modulus of Elasticity	29,400,000 Pounds Per Square Inch
Rockwell Superficial Hardness	N15-71.5

Blasting Conditions

Kinetic considerations would indicate that the degree of surface deformation could be expected to depend upon the angle of blast, upon the blasting air pressure, and upon the blasting medium. As the number of such possible combinations is very large, it was thought

*Determined at Fritz Laboratory, Lehigh University.

best to begin the blasting investigation by holding the pressure and blast angle constant, and to experiment with three sand media, namely, round sand, sand dust, and a mixture of sand dust and carborundum; also round steel shot of various sizes, steel grit, and various mixtures of steel shot and grit. In this way the subsequent investigation in sand and shot blasting could be limited to one material in each group of blasting media, thus allowing the angle and pressure of the blasting medium to be varied.

Sand Blasting—Groups of specimens were blasted with round (a) Ottawa sand, (b) sand dust passing through an 80-mesh sieve, and (c) a mixture of approximately 50 per cent sand dust and 50 per cent crushed carborundum. Figs. 3, 4, and 5 show the particle size of these sands at a magnification of 16 diameters.

The technique followed in blasting was to pass the sand stream lengthwise along the specimen. The hose nozzle was approximately 12 inches from the specimen. In the preliminary tests the sand stream was always perpendicular to the surface of the specimen. This angle was varied in later tests. A blasting pressure of 65 pounds per square inch was used for the sand dust and the mixture of sand dust and carborundum. Because of mechanical difficulties, it was necessary to use 80 pounds per square inch for the round sand.

To remove the oxide scale completely, it was necessary to blast each side of the specimen with two passes for each of the sand media used. The hose nozzle moved approximately 1 foot per second.

Shot and Grit Blasting—In addition to sand blasting, groups of specimens were blasted with various sizes of round steel shot, steel grit, and mixtures of round shot and grit. The type of steel blasting medium used for each group of specimens is shown below:

Group 1—Mixture—No. 26 Steel Shot
No. 50 Steel Grit
Group 2—Mixture—75 Per Cent No. 90 Steel Grit
25 Per Cent No. 60 Steel Grit
Group 3—Mixture—75 Per Cent No. 60 Steel Grit
25 Per Cent No. 90 Steel Grit
Group 4—Mixture—No. 26 and No. 40 Steel Shot
No. 90 Steel Grit
Group 5—No. 40 Round Steel Shot

Figs. 6, 7, 8, 9, and 10 show photomacrographs of the various steel media used.

The technique followed in shot blasting was identical with that used in sand blasting in that the blast stream was always perpendicular to the surface of the specimen, with the hose nozzle approximately

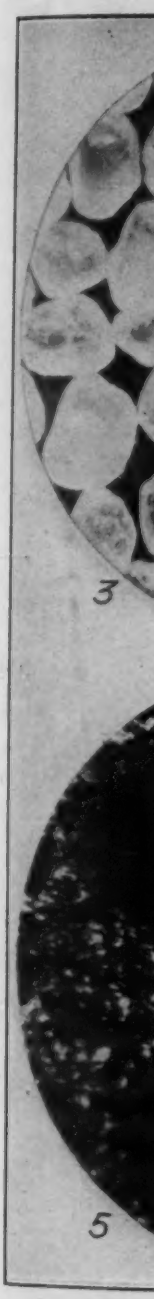


Fig. 5—Ph
Dust. × 16.
Fig. 6—Ph
× 15.

12 inches d
pressure of
steel media

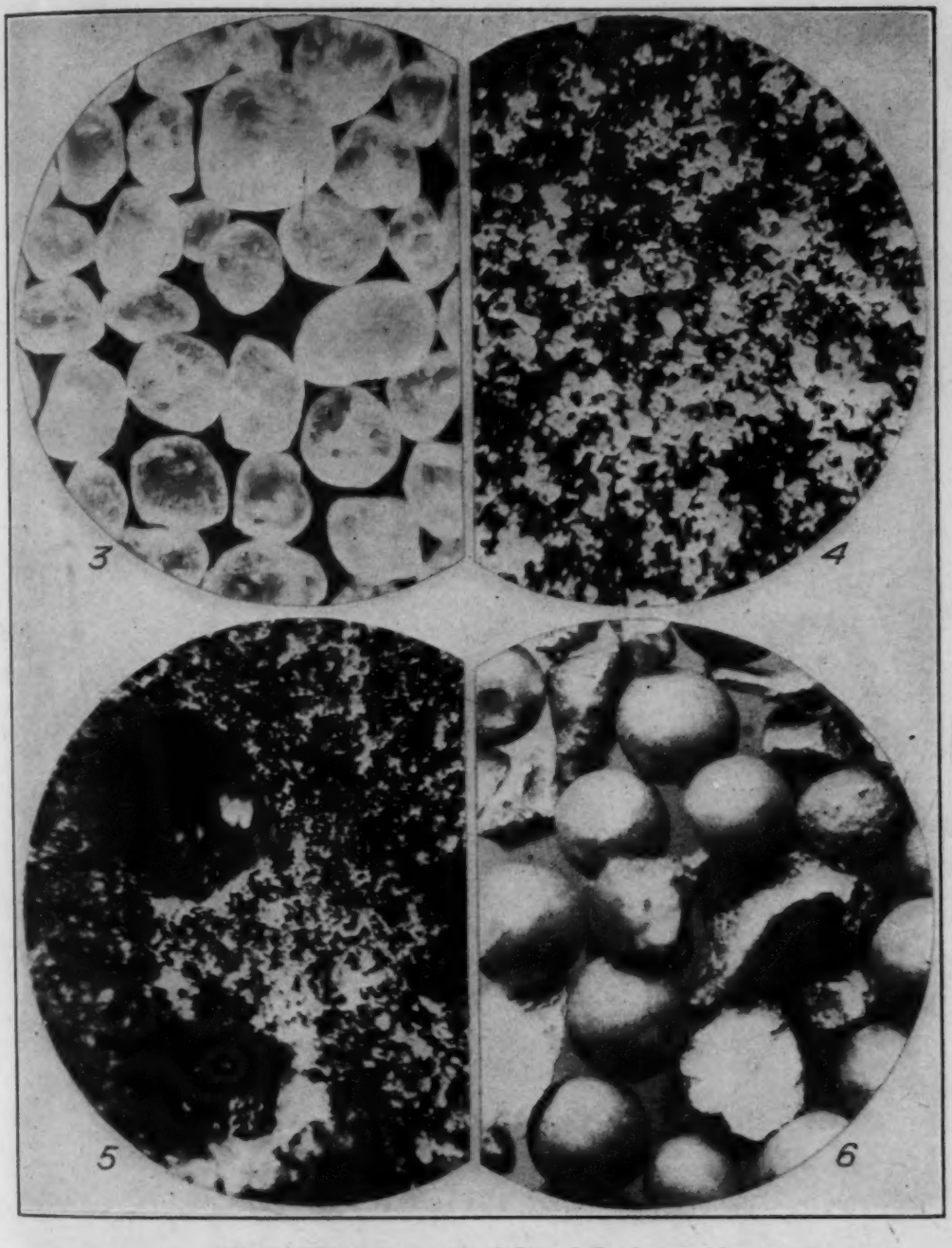


Fig. 3—Photomacrograph of Round Sand. × 16.
Fig. 4—Photomacrograph of Sand Dust. × 16.
Fig. 5—Photomacrograph of Mixture—50 Per Cent Carborundum, 50 Per Cent Sand Dust. × 16.
Fig. 6—Photomacrograph of Mixture—No. 26 Round Steel Shot, No. 50 Steel Grit. × 15.

12 inches distant, moving at about 1 foot per second. A blasting pressure of 80 pounds per square inch was employed for all types of steel media used.

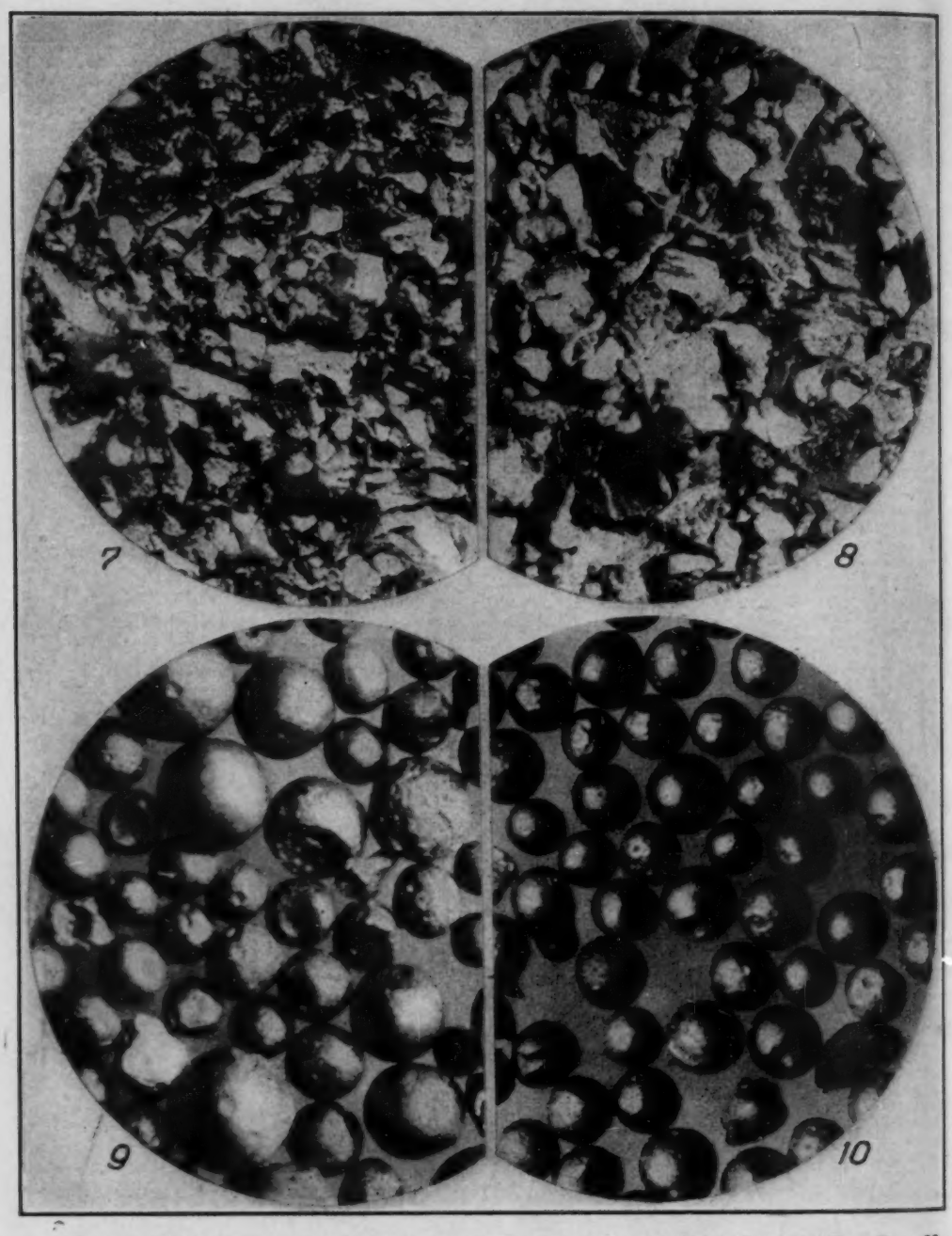


Fig. 7—Photomacrograph of Mixture—75 Per Cent No. 90 Steel Grit, 25 Per Cent No. 60 Steel Grit. × 15.

Fig. 8—Photomacrograph of Mixture—75 Per Cent No. 60 Steel Grit, 25 Per Cent No. 90 Steel Grit. × 15.

Fig. 9—Photomacrograph of Mixture—No. 26 and No. 40 Round Steel Shot, No. 90 Steel Grit. × 15.

Fig. 10—Photomacrograph of No. 40 Round Steel Shot. × 15.

Angle Blasting with Sand Dust—As shown in Fig. 11, it was found that in the sand blasted group, specimens blasted with sand dust had the highest endurance limit. Thus for further studies the

sand dust was adopted since it promised best results. To investigate the effects of blast pressure and angle of blast variations, specimens were blasted with sand dust at pressures of 35, 65, and 80 pounds per square inch, at angles of 90, 75, 45, and 20 degrees for each pressure. A specially designed jig was employed to hold the specimen firmly with the longitudinal axis of the specimen at any desired angle to the sand stream. The angle to the transverse axis was in all cases 90

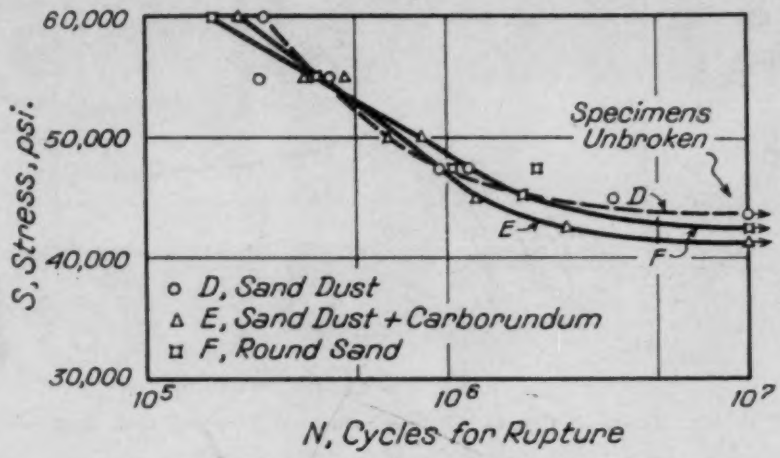


Fig. 11—S-N Curves of Specimens Blasted with Sand Media.

degrees. The hose nozzle at all times was approximately 12 inches from the surface of the specimen and two passes were sufficient to remove the oxide scale. The speed of blasting was one foot per second as in previous cases.

Acid Pickling—For the purposes of comparison, a set of specimens was pickled in 5 per cent sulphuric acid at a temperature of 150 degrees Fahr. by a commercial concern engaged in such work. To eliminate hydrogen embrittlement the specimens were heated at 212 degrees Fahr. for two hours.

Endurance Limit and Surface Notch Results

The endurance limit of the material in the as-received condition was 47,500 pounds per square inch, which was approximately 42 per cent of the ultimate tensile strength. The complete fatigue curve is shown in Fig. 12. This value of 47,500 pounds per square inch, therefore, represents a basis upon which to compare fatigue limits of other specimens that have had their surfaces altered by notching, surface cold working, or a combination of both.

Acid pickling, which produces no surface cold work, caused a drop of 5000 pounds per square inch in the fatigue limit as shown in Fig. 12. This drop was probably due to the severe notch condition as shown in Fig. 13. Fig. 13 and all similar photomicrographs were taken at an edge of the specimen, parallel to the longitudinal axis. At least 2 inches of the specimen were examined microscopically and,

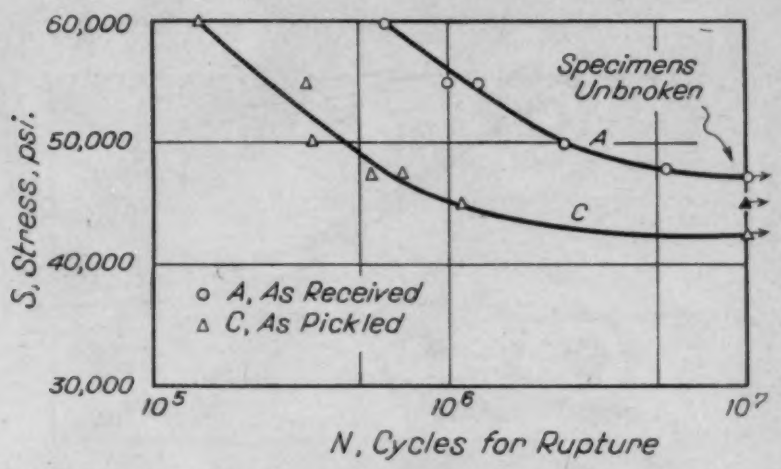


Fig. 12—S-N Curves of Specimens as Received and Acid Pickled.

in the opinion of the authors, the photomicrographs represent the average notch development.

Sand Blasting—In Fig. 11, the endurance limits of the specimens blasted with the three sand media were shown to be very close together, all being lower than the fatigue limit of the material as received. The notch condition resulting from this blasting is shown in Figs. 14, 15, and 16. However, since the specimens blasted with sand dust had a fatigue limit 1000 pounds per square inch higher than those blasted with round sand and with sand dust and carborundum, this blasting medium was chosen for further study which consisted of varying the angle and pressure. The variation of fatigue life with blast angle for any given blast pressure was found to be considerable. The results of this work are shown in Figs. 17 and 18.

At 65 pounds per square inch pressure the endurance life of the specimens was considerably influenced by the angle of blast as shown in Figs. 17 and 18. Furthermore, at this pressure a life practically as high as at other pressures was obtained. Since these curves, however, do not indicate true fatigue strength, two complete fatigue curves were run for the blasting pressure of 65 pounds per square inch at angles of 20 and 90 degrees. It was found that at an angle

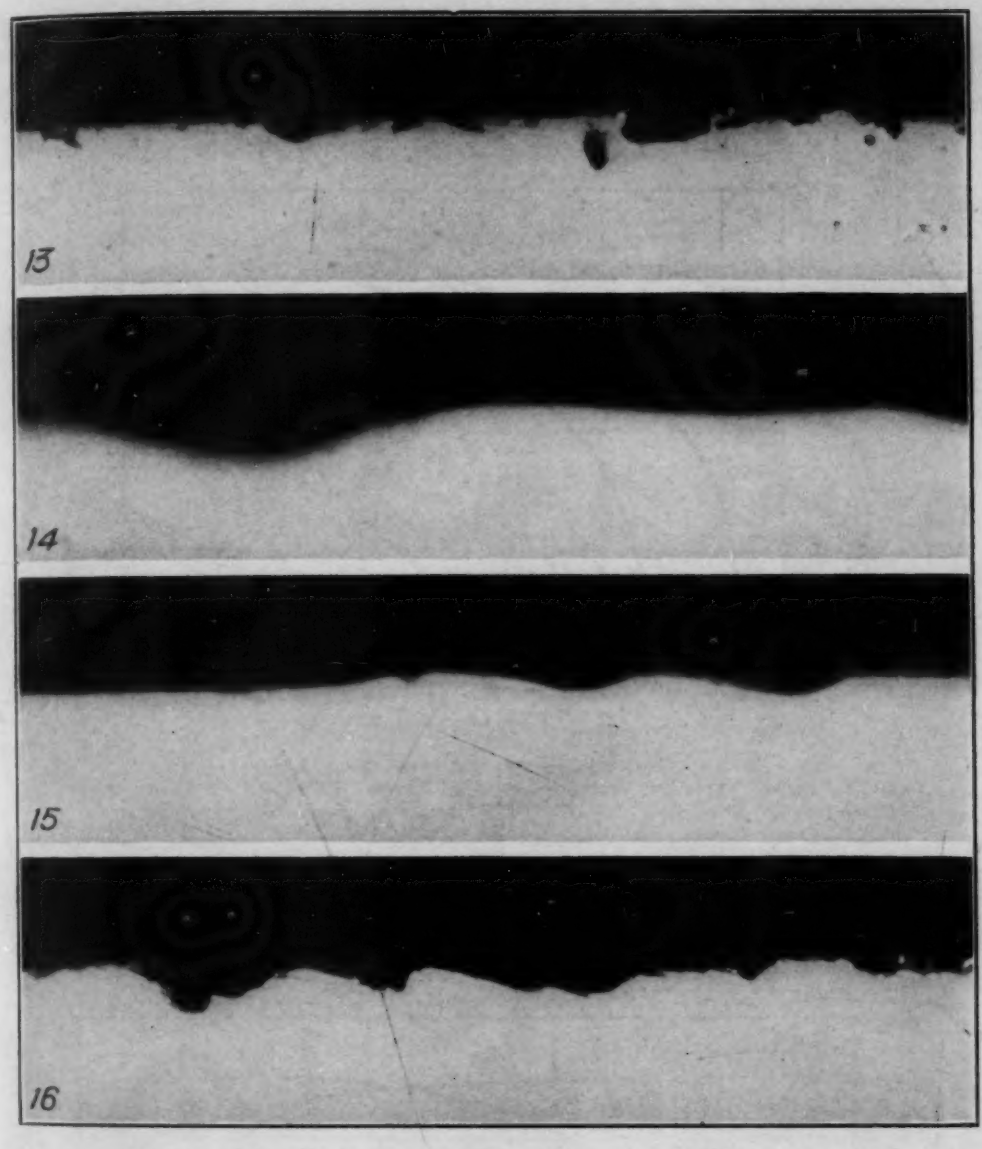


Fig. 13—Photomicrograph of Steel Specimen Acid Pickled. × 350.
Fig. 14—Photomicrograph of Steel Specimen Blasted with Round Sand. × 350.
Fig. 15—Photomicrograph of Steel Specimen Blasted with Sand Dust. × 350.
Fig. 16—Photomicrograph of Steel Specimen Blasted with Sand Dust and Carborundum Mixture. × 350.

of 90 degrees the fatigue limit was 43,500 pounds per square inch, and at 20 degrees, 37,500 pounds per square inch as shown in Fig. 19.

Shot and Grit Blasting—The fatigue limits of specimens blasted with the two different mixtures of No. 90 and No. 60 steel grits were 45,000 pounds per square inch as shown in Fig. 20. Out of this group, specimens blasted with a larger proportion of No. 60 steel grit had a slightly more severe notch condition than those blasted with a smaller amount. This is shown in Figs. 22 and 23.

Specimens blasted with No. 40 round steel shot had a fatigue limit of 55,000 pounds per square inch and those blasted with a mixture of No. 26 and No. 40 steel shot and No. 90 steel grit had a

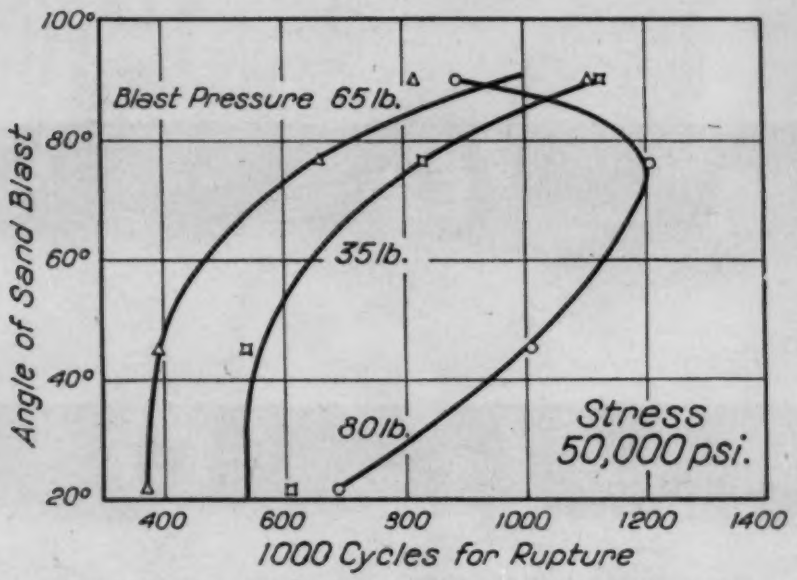


Fig. 17—Curves Showing the Effect of Blast Angle and Blast Pressure Variation Relative to Endurance Strength. Blasting Medium—Sand Dust.

fatigue limit of 52,500 pounds per square inch, an increase in fatigue strength over the material as received of 7500 and 5000 pounds per

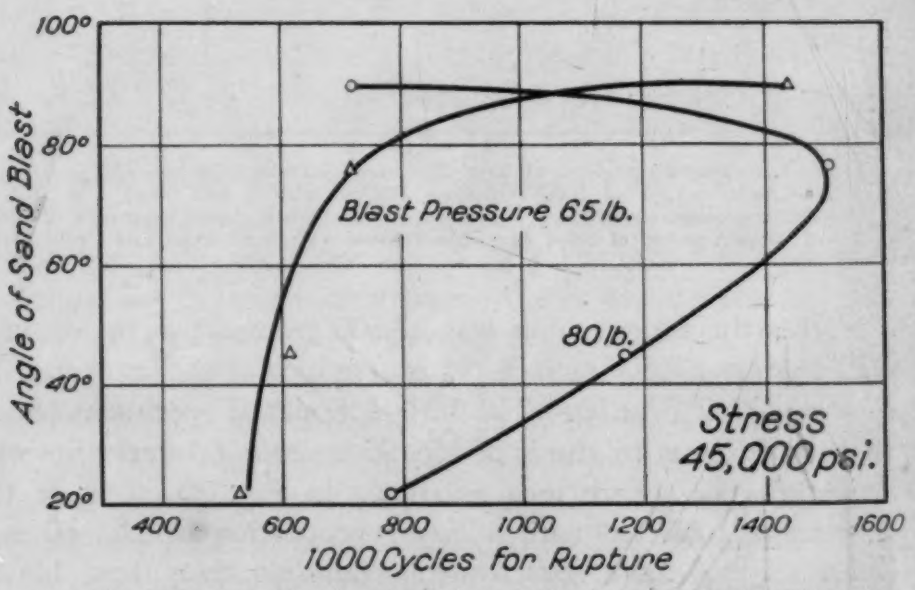


Fig. 18—Curves Showing the Effect of Blast Angle and Blast Pressure Variation Relative to Endurance Strength. Blasting Medium—Sand Dust.

square inch respectively. These fatigue curves are shown in Fig. 21. This increase in fatigue strength is indicated by the smooth surface condition as shown in Figs. 24 and 25. In addition, the relative

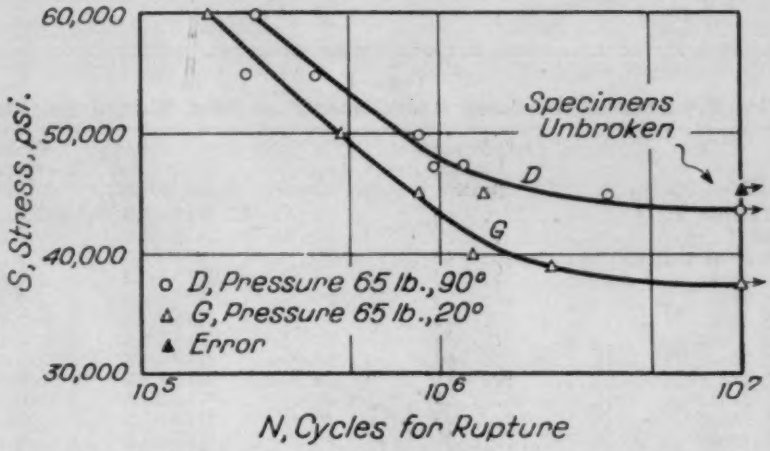


Fig. 19—Complete S-N Curves of Specimens Blasted with Sand Dust at Two Extreme Angles—90 and 20 Degrees.

amounts of surface cold working as shown in Table II probably contributes toward a greater endurance limit.

Specimens blasted with a mixture of No. 26 steel shot and No.

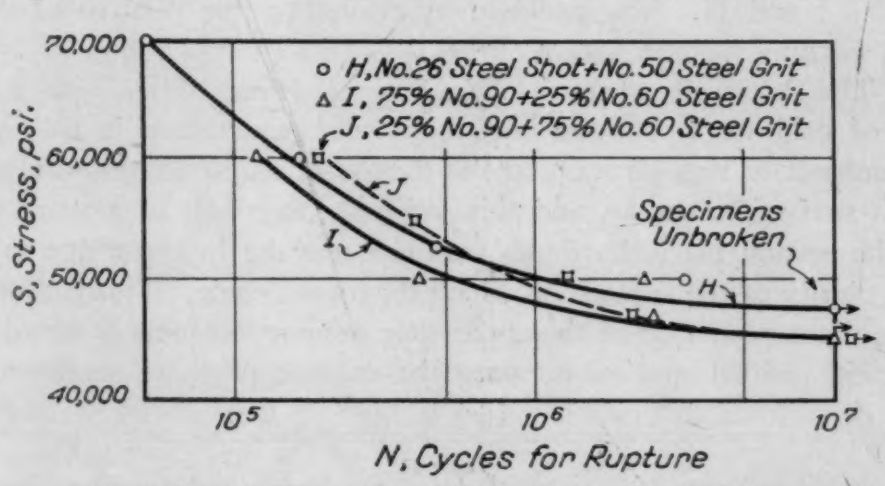


Fig. 20—S-N Curves of Specimens Blasted with Steel Media.

50 steel grit had, as indicated in Fig. 20, the same fatigue limit as the material as received. The surface notch condition resulting from this particular blasting is shown in Fig. 26.

Discussion of Results

This study of the effects of different cleaning methods on fatigue

strength has been attacked from the standpoint of surface hardness and surface notches.

Decrease in the thickness of the beam section due to removal of surface material by blasting is negligible, as indicated by the close

Table I

Rockwell Superficial Hardness Measurements on Sand Blasted Specimens

Blasting Medium	Pressure Pounds Per Square Inch	Angle of Blast	Superficial Hardness	Thickness of Specimen Inches
Sand Dust	65	90	N15-69.5	0.1245
Round Sand	80	90	N15-66.5	0.1242
Sand Dust and Carborundum	65	90	N15-67.0	0.1245
Sand Dust	80	90	N15-70.0	0.1245
Sand Dust	80	75	N15-69.5	0.1250
Sand Dust	80	45	N15-69.5	0.1245
Sand Dust	80	20	N15-68.5	0.1245
Sand Dust	65	90	N15-69.5	0.1245
Sand Dust	65	75	N15-69.0	0.1245
Sand Dust	65	45	N15-68.5	0.1245
Sand Dust	65	20	N15-67.5	0.1245
Sand Dust	35	90	N15-69.5	0.1245
Sand Dust	35	75	N15-68.5	0.1248
Sand Dust	35	45	N15-68.5	0.1245
Sand Dust	35	20	N15-66.5	0.1245
Material "As-Received"	..	..	N15-71.5	0.1250
Specimens Acid Pickled	..	..	N15-71.5	0.1245

agreement between micrometer readings of thickness indicated in Tables I and II. The problem of evaluating the relative effect of cold working is not a simple one.

The Rockwell superficial hardness test is certainly a valid measure of cold work, but the hardness readings obtained in this work are subject to two errors. In the first place, the hardness drops off from surface to center, and this gradient may well be a sharp one. In the second place, hardness readings may be in error due to the irregularity of the surface on which they were made. This is thought to be the explanation of the apparently greater hardness obtained for the acid pickled specimens, since the surface of these specimens is

Table II

Rockwell Superficial Hardness Measurements on Steel Grit and Shot Blasted Specimens

Blasting Medium	Pressure Pounds Per Square Inch	Angle of Blast	Superficial Hardness	Thickness of Specimen Inches
Mixture—No. 26 Steel Shot No. 50 Steel Grit	80	90	N15-71.0	0.1240
75 Per Cent No. 90 Steel Grit 25 Per Cent No. 60 Steel Grit	80	90	N15-69.0	0.1240
75 Per Cent No. 60 Steel Grit 25 Per Cent No. 90 Steel Grit	80	90	N15-69.5	0.1240
No. 40 Steel Shot	80	90	N15-72.0	0.1240
Mixture—No. 26 and No. 40 Steel Shot No. 90 Steel Grit	80	90	N15-71.5	0.1245

much less irregular as can be seen by the unaided eye. The superficial hardness values in Table I and Table II are the average of ten hardness measurements. Since each set of ten readings was in very close agreement, the authors believe the surface hardness values are valid for comparative work.

This belief is strengthened by the observation that the hardness of the sand blasted specimens increases as the blasting angle approaches 90 degrees. If the mass of a sand particle is m and the component of velocity perpendicular to the specimen surface is v_1,

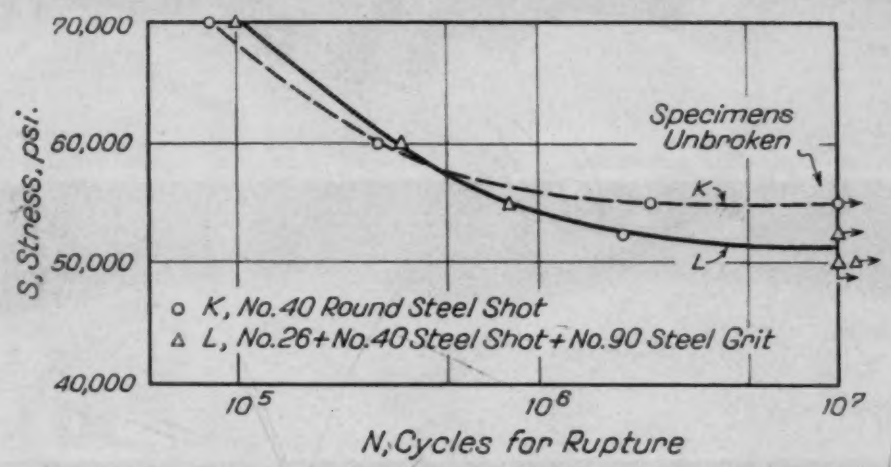


Fig. 21—S-N Curves of Specimens Blasted with Steel Media.

then the kinetic energy of the particle in a direction to the specimen surface is $\frac{1}{2}mv_1^2$. At the instant of contact, $v = O$, and energy equal to $\frac{1}{2}mv_1^2$ is absorbed by the particle and specimen. Some fraction of this energy is used in permanently deforming the surface of the steel. Since this energy increases continuously from 0 degree to a maximum at 90 degrees, it would be expected that the hardness would increase to a maximum at this angle. This is exactly what the hardness readings show. An increase in blasting pressure, other things remaining constant, obviously increases the hardness.

The determination of notch effect, unlike that of hardness, is purely a matter of personal judgment. The theoretical notch concentration factor is dependent upon the depth and radius of curvature of the base of the notch. McAdam and Clyne[3] express this notch

[3]McAdam and Clyne, "Influence of Chemically and Mechanically Formed Notches on Fatigue of Metals," Research Paper No. R.P. 725. National Bureau of Standards.

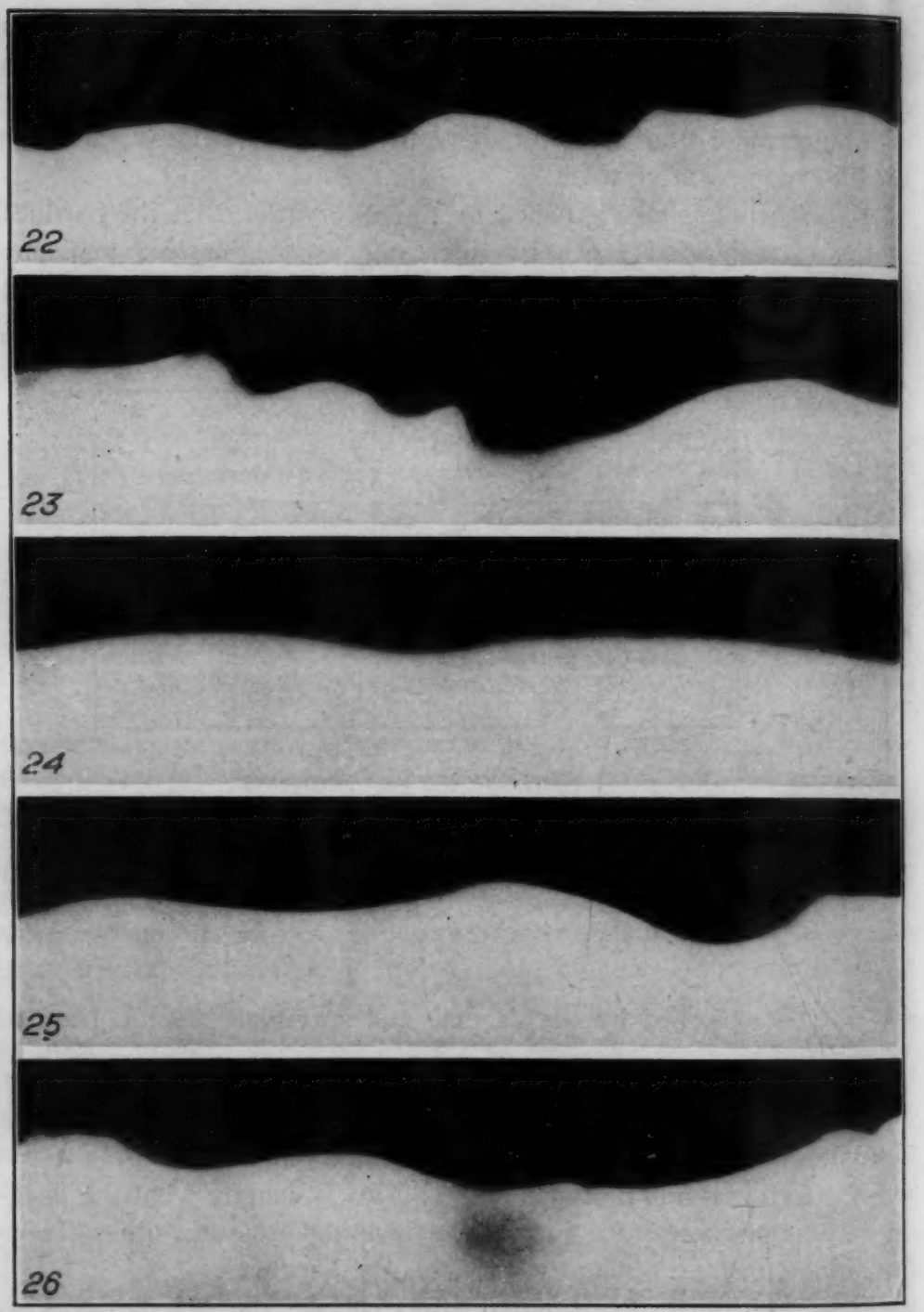


Fig. 22—Photomicrograph of Steel Specimen. Blasting Medium—75 Per Cent No. 90 Steel Grit, 25 Per Cent No. 60 Steel Grit. × 350.

Fig. 23—Photomicrograph of Steel Specimen. Blasting Medium—75 Per Cent No. 60 Steel Grit, 25 Per Cent No. 90 Steel Grit. × 350.

Fig. 24—Photomicrograph of Steel Specimen. Blasting Medium—No. 26 and No. 40 Round Steel Shot, No. 90 Steel Grit. × 350.

Fig. 25—Photomicrograph of Steel Specimen. Blasting Medium—No. 40 Round Steel Shot. × 350.

Fig. 26—Photomicrograph of Steel Specimen. Blasting Medium—No. 26 Round Steel Shot, No. 50 Steel Grit. × 350.

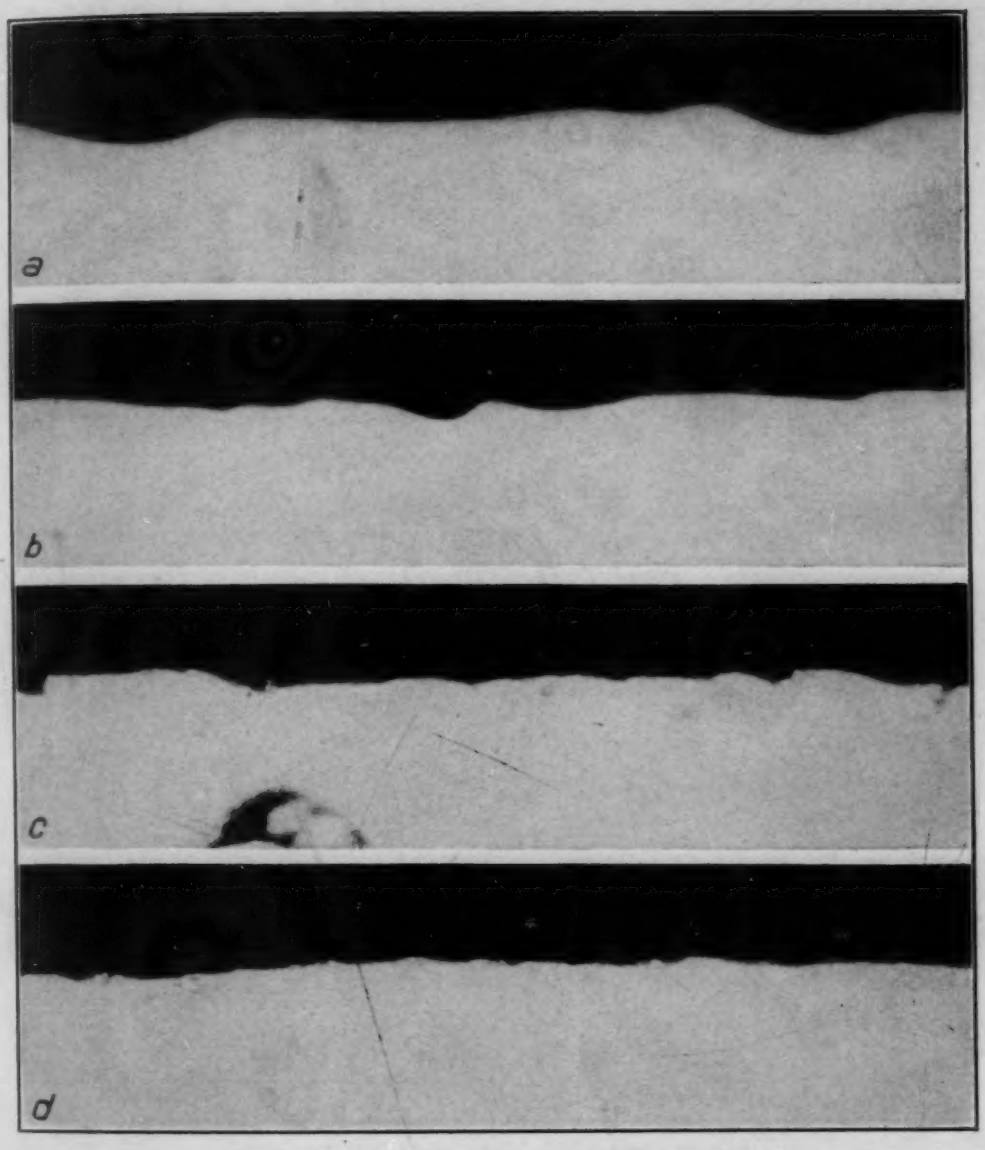


Fig. 27—Photomicrographs of Steel Specimens.

(a) Blast Pressure—35 Pounds Per Square Inch. Angle of Blast—90 Degrees.
(b) Blast Pressure—35 Pounds Per Square Inch. Angle of Blast—75 Degrees.
(c) Blast Pressure—35 Pounds Per Square Inch. Angle of Blast—45 Degrees.
(d) Blast Pressure—35 Pounds Per Square Inch. Angle of Blast—20 Degrees.
Blasting Medium—Sand Dust

concentration factor by the formula $1 + 2\sqrt{\frac{d}{r}}$, where d = depth of notch and r = radius of curvature of the notch root. The difficulty of applying this formula is obvious, as the photomicrographs show the notches to be very irregular. Consequently, no attempt has been made to obtain actual measurements. This formula is useful, how-

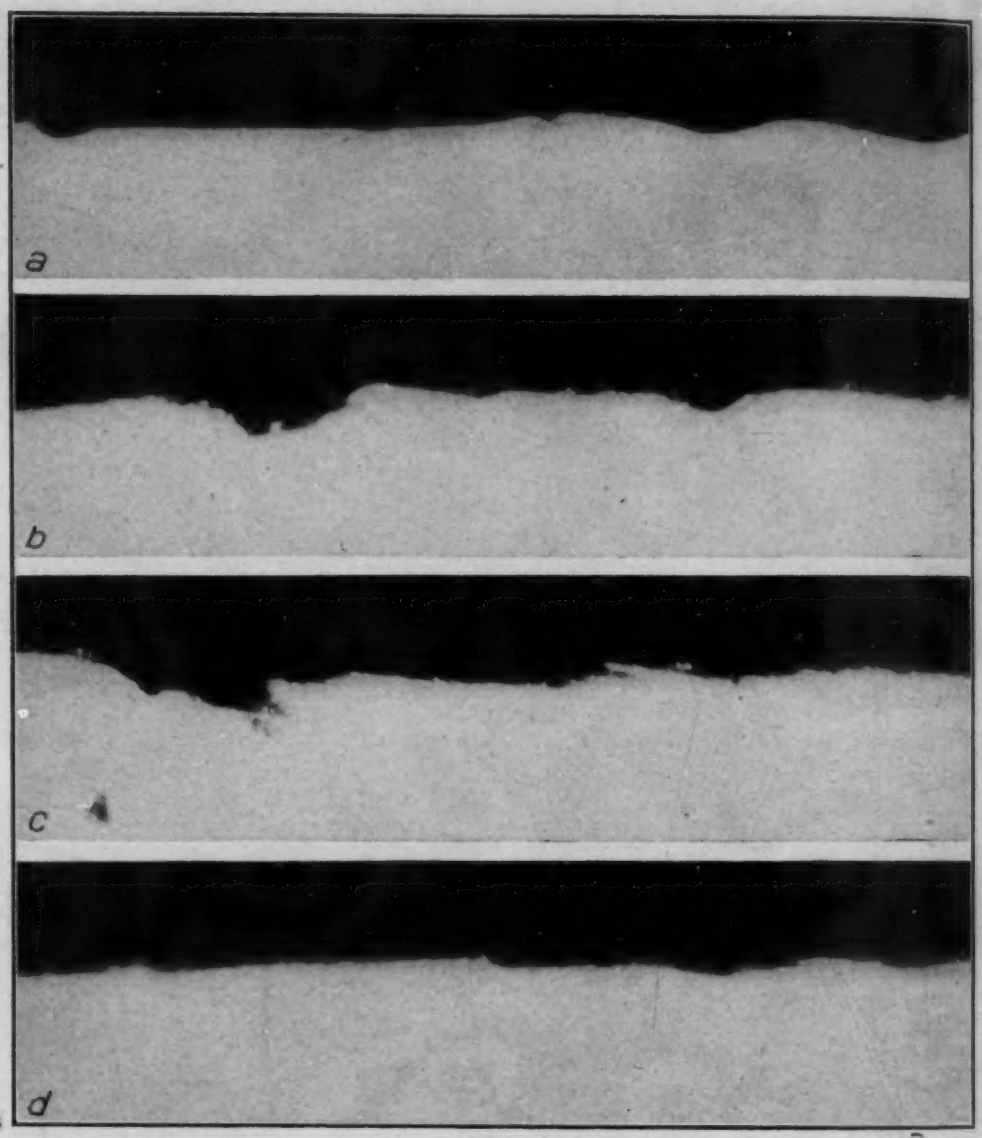


Fig. 28—Photomicrographs of Steel Specimens.
(a) Blast Pressure—65 Pounds Per Square Inch. Angle of Blast—90 Degrees.
(b) Blast Pressure—65 Pounds Per Square Inch. Angle of Blast—75 Degrees.
(c) Blast Pressure—65 Pounds Per Square Inch. Angle of Blast—45 Degrees.
(d) Blast Pressure—65 Pounds Per Square Inch. Angle of Blast—20 Degrees.
Blasting Medium—Sand Dust

ever, as a general guide. It seems obvious, from an investigation of these photomicrographs, that there is a general tendency for the notches to become more and more severe as the blasting pressure increases and the angle of blasting approaches 90 degrees.

The data seem to indicate that the degree of cold work and the severity of the notches, as shown in Figs. 27, 28, and 29, both increase with angle and pressure of blast. Since one is beneficial and the other

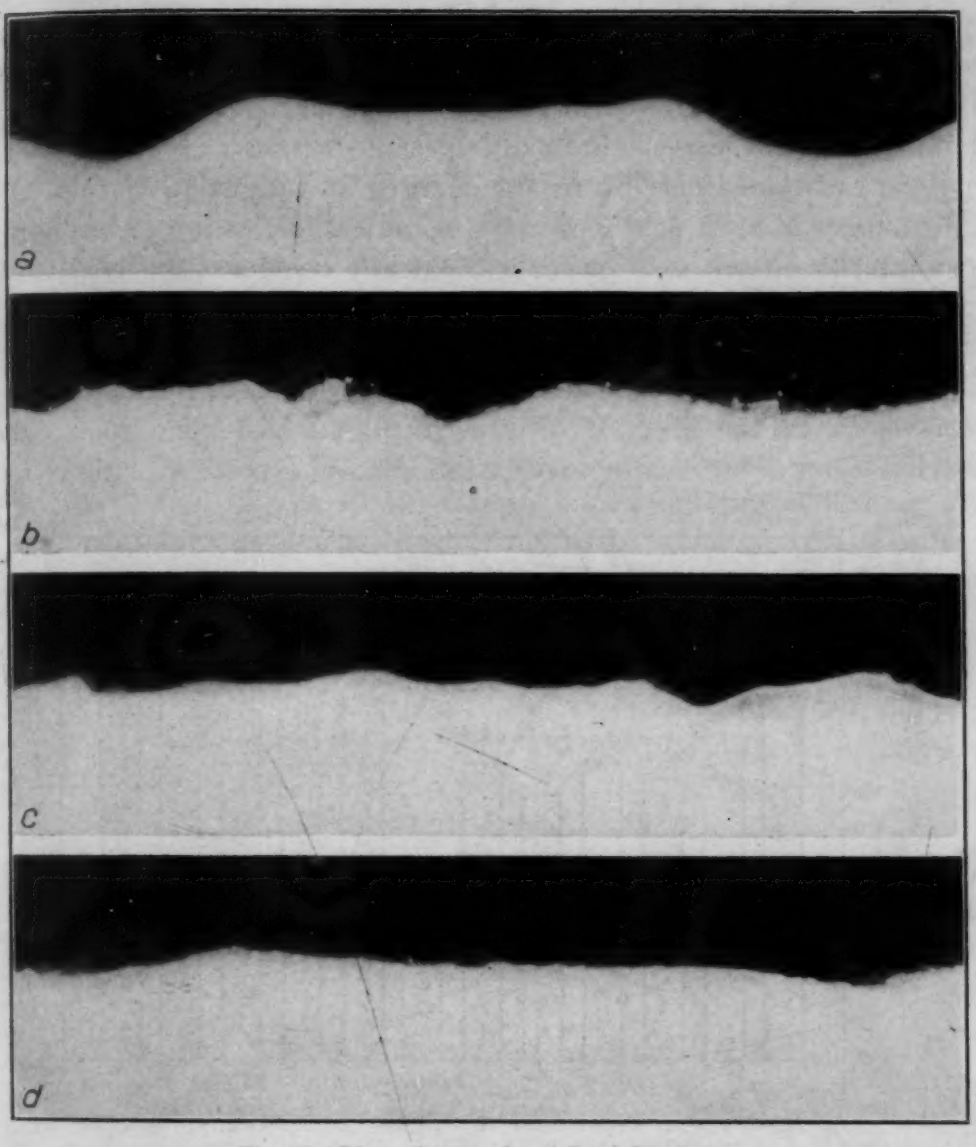


Fig. 29—Photomicrographs of Steel Specimens.
(a) Blast Pressure—80 Pounds Per Square Inch. Angle of Blast—90 Degrees.
(b) Blast Pressure—80 Pounds Per Square Inch. Angle of Blast—75 Degrees.
(c) Blast Pressure—80 Pounds Per Square Inch. Angle of Blast—45 Degrees.
(d) Blast Pressure—80 Pounds Per Square Inch. Angle of Blast—20 Degrees.
Blasting Medium—Sand Dust.

deleterious, it is obvious why the curves in Figs. 17 and 18 show a maxima or minima between 20 and 90 degrees.

Specimens blasted with sand dust at a pressure of 65 pounds per square inch at an angle of 20 degrees gave a fatigue limit of 37,500 pounds per square inch with a superficial hardness of N15-67.5 and a relatively good surface condition as shown in Fig. 28d. Blasting under identical conditions, except that the angle of blast was 90 de-

grees, gave a fatigue limit of 43,500 pounds per square inch with a hardness of N15-69.5 and a poorer surface condition, as shown in Fig. 28a. Apparently the increased surface hardness has more than compensated for the notch condition.

As mentioned heretofore, the decrease in fatigue strength of the rolled material after acid pickling is doubtless due to the severe notch condition as shown in Fig. 13, without any compensating cold work effect.

The increase in fatigue life of specimens blasted with steel media is perhaps due to the comparatively greater amount of surface cold working with the absence of a harmful surface condition. The notches caused by blasting with steel media, especially with round

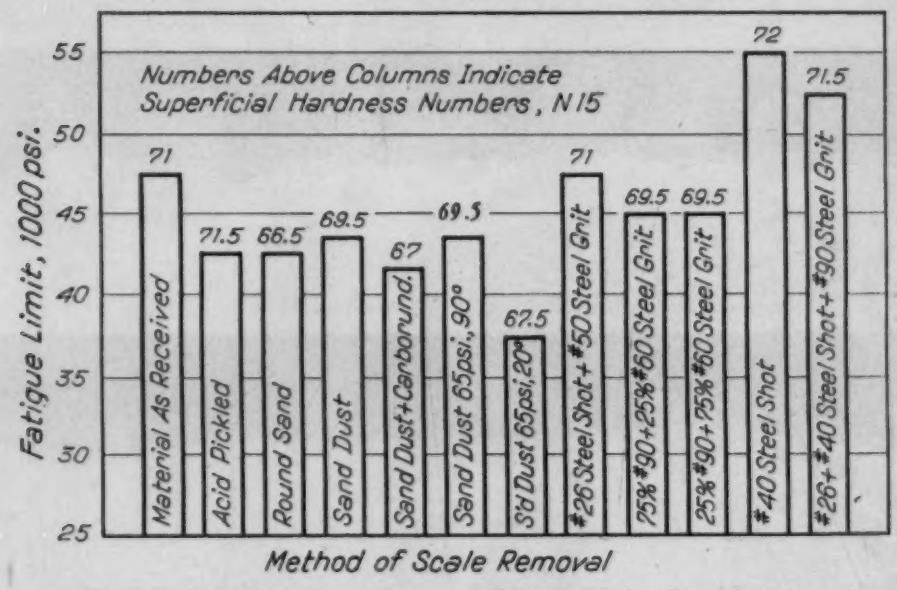


Fig. 30—Graphical Presentation of Fatigue Limits Resulting from Descaling by Various Methods.

shot, were not nearly as sharp as those caused by blasting with steel grit and the various sand media. Consequently, it was to be expected that a higher fatigue life should result.

The larger the size of steel shot used, other things remaining constant, the greater will be the amount of cold working, as indicated in Table II. However, it was the authors' opinion, based on visual examination, that the larger the shot used, the greater the tendency for the specimen to warp in blasting. Furthermore, when the shot used was too large, the scale was not removed but pounded into the base metal.

Conclusions

The results of this work are summarized in Fig. 30, which shows graphically the fatigue limits obtained by descaling with various mechanical cleaning methods. Since the number of combinations of pressure, angle, and type of blasting medium used is infinite, no universally valid conclusions may be drawn. The data obtained are therefore not complete, but for the steel and blasting methods used in this investigation the following views are strongly favored:

1. The endurance limit of steel cleaned by sand blasting varies very little with the three types of sand used, but does vary considerably with change in the combination of pressure and angle of blast.
2. There is but slight difference between the endurance limit obtained after sand blasting with the most favorable combination of angle and pressure and that obtained after a commercial sulphuric acid pickle.
3. Blasting with steel grit, shot, or mixtures of the two is definitely superior to sand blasting or the usual sulphuric acid pickle in effect on the fatigue limit. Here the blasting medium is extremely important and, with proper selection, a fatigue strength can be had which is considerably higher than that obtainable with the other two methods.
4. The fatigue strength obtained by blasting with either sand or steel media is the result of two opposing surface effects, cold working and notching.

Acknowledgments

The authors wish to thank Professors Bradley Stoughton, Gilbert E. Doan, Allison Butts, and Mr. Wilber E. Harvey for counsel and encouragement throughout the course of this investigation. The project was supported by funds of the New Jersey Zinc Company Research Fellowship.

DISCUSSION

Written Discussion: By W. R. Bloxdorf, metallurgist, Macwhyte Co., Kenosha, Wis.

The authors' paper is very interesting and certainly deserves a distinct position among the many contributions to the study of fatigue. Surface conditioning, or preparation, is a phase of metal treatment with which all are more or less concerned, and its relation to fatigue failures is one of great importance. Although the data presented in this present paper are limited to the results of

work done thus far on one type of steel in a particular structural condition, it is very valuable and should promote further work of the same nature on other steels in various structural states.

The fatigue testing machine used in this work is of interest to me. I presume that actual failure of the specimens occurred at or very near their points of contact with the oscillating center grips. At the end of each test, I would like to know whether or not any marking was noticed on the surface of the specimen at its point of contact with the grips. If there was, and if ultimate fracture occurred at this point, were any microscopic studies made of the specimens to determine whether or not this marking was associated with any surface and superficial subsurface flow of the grains of the steel? If such flow were detected, then it would indicate that, during the course of the test, the specimen was being subjected to a very highly localized cold working. This cold working would gradually build up the specimen's resistance to fatigue at this particular point and then, after a maximum had been reached, an actual embrittling of the surface metal would occur rendering the surface very susceptible to cracking. This marking at the point of contact, if it occurred at all, I consider to be primarily a function of the resistance which the surface grains offer to deformation and of the effect of any medium present on the surface which would serve to protect the grains from deforming forces. When one applies this line of thought to the study presented in this paper, it appears that the acid-pickled specimens would be most susceptible to surface deformation, that the scale present on the "as received" specimens would afford protection against deformation for a certain length of time during the test, and that the specimens whose surface had been hardened through cold work induced by blasting would offer resistance to deformation for a limited time during the test. Thus, this surface marking would have the greatest effect upon the acid-pickled specimens with the result that their apparent fatigue values would be lowest. I offer this thought merely with the idea in mind that it may probably be a factor in obtaining comparative fatigue values.

Were any microscopic studies made of the surface of the "as received" specimens with the scale intact? I ask this question because I was wondering whether or not the appearance of the junction of the scale with the steel bore any similarity to the appearance of the surface of the acid-pickled specimen shown in Fig. 13. If it did, then I believe that the rather rough appearing surface was due to the mechanism of scale formation during heat treatment and not to faulty pickling procedure.

Referring to the description of the procedure employed in pickling the specimens, do the authors know how long the specimens were subjected to the pickling solution? Did the pickling solution contain an inhibitor and how much inhibitor was present? What was the ferrous sulphate content of the solution? All of these factors serve to affect the quality and character of the pickled surface, and, if the magnitude of their effects insofar as influencing the fatigue properties of the pickled member is concerned has not been studied, I truly believe that such an investigation would yield some valuable data. We have recently made studies along these lines, and, while the work thus far has been quite limited, the results obtained have been rather enlightening.

Upon studying the photomicrographs illustrating the notches and surface

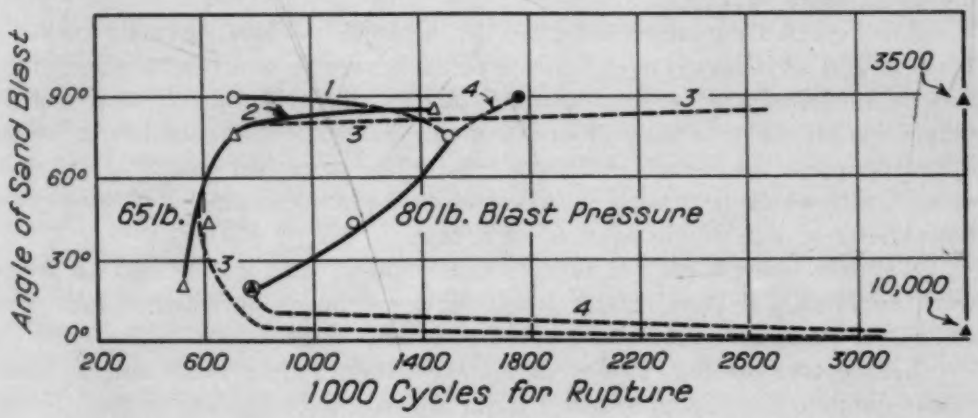
irregularities produced by the various blasting procedures, the question came to my mind as to whether or not there was any apparent relation between the depth and shape of the notch and the orientation of the surface grains. Were any studies made to determine the possibility of such a relationship? Applied to lower carbon steels in the annealed or normalized condition, I believe that an investigation of this sort would prove valuable.

The fact that an increase in the angle of blast up to 90 degrees results in an increase in surface hardness is interesting. Have the authors determined what the maximum surface hardness obtainable through blasting is? Although very remote, the possibility exists of cold working the surface of the metal to the point of embrittlement, thereby lowering its fatigue properties. However, I presume that before this point was reached, the surface would become very rough and unsuitable which in itself would render the metal quite poor from a fatigue resisting standpoint.

In the authors' opinion, based upon experience with blasting procedure, would this be true?

Written Discussion: By W. E. Harvey, John A. Roebling's Sons Co., Trenton, N. J.

To welcome a new author to the American Society for Metals is always a pleasure. To find these new contributors young men is more than simply a pleasure. Satisfaction is found because it is upon these younger men's efforts that the future of any technical society is dependent. Upon their genius rests



the continuance of able investigations of the too many unsolved problems facing not only the metallurgist of the world but every engineer in industry.

The question of sand blasting versus fatigue studies while not new deserved richly the attentions the authors have rendered it. We are indebted to the authors for reviving an interesting study.

Several years ago a manufacturing firm on a laboratory scale used sand blasting and scrubbing as a surface preparation for wire prior to electroplating with zinc. The experiment was very successful and the electrodeposit was beautifully adherent to the wire and the deposit was very uniform. Unfortunately the cost angle prevented its commercial success. It does indicate, however, that sand blasting can be used very effectively in the preparation of surface prior to electroplating.

Examining Figs. 17 and 18 offers the interpretation that the endurance life of sand blasted steel at any given nominal testing stress is, in general, improved by an increase in the angle of blast pressure. This conclusion is true. However it will be noticed that the ordinate of the curve does not extend to zero. Thus the curve does not indicate the relative damage done to the steel by the blasting operation. Theoretically with a zero angle of blast pressure the surface of the tested steel would be unaffected by the sand blasting. Thus a zero reading for the ordinate can be taken as the unaffected or as-received specimen life at the nominal stresses under consideration. The life of the as-received specimen as tested at 50,000 pounds per square inch was approximately 2,500,000 cycles as taken from Fig. 12. Likewise from the same Fig. 12 the life of the as-received specimen tested at 45,000 pounds per square inch was indefinite ($>10^7$ cycles) since the fatigue limit of the steel is 47,500 pounds per square inch. The liberty of replotting part of the authors' data with these additional zero angle values has been taken and the curves are shown in the accompanying graph. The points added to the curve have been darkened to differentiate from the original points of the authors used in establishing their curves. Only Fig. 18 of the authors' paper has been reproduced although the data are available to add the additional points to Fig. 17. Thus a net damage curve is presented which illustrates the life shortening at the testing stress of the as-received material after it has been subjected to sand blasting. The authors in their text announce this shortening of life by sand blasting but the graph shown herewith illustrates the effect more strikingly.

The reversed curvature exhibited by the 80-pound blast pressure curves in Figs. 17 and 18 is impressive. In each of the curves in which a reversed curvature is exhibited the reversal of curvature is caused by the 90-degree angle points. With the exception of one point on each curve the remainder of the test data follow an entirely different trend. The mere fact that it is one point in each case which is causing the reversal of curvature compels one to question the validity of that single point in each case.

I should like to ask the authors if the curves in Figs. 17 and 18 are or were established by test results from single specimens or whether each point on the curves is a representative value of several tests.

Let us turn to Fig. 19 for a moment. Immediately there will be found values exhibited by the curves of Fig. 19 which can be applied to Figs. 17 and 18. Again this discussion will be limited to Fig. 18 although the same interpretation could be applied to Fig. 17. The following values may be taken from Fig. 19:

65-Pound Pressure, 90-degree angle, 45,000 psi ..... 3,500,000 cycles
65-Pound Pressure, 20-degree angle, 45,000 psi ..... 775,000 cycles

The authors in Fig. 18 show the following data for similarly tested specimens:

65-Pound Pressure, 90-degree angle, 45,000 psi ..... 1,450,000 cycles
65-Pound Pressure, 20-degree angle, 45,000 psi ..... 525,000 cycles

Thus with the 90-degree angle specimens there is between two specimens tested under similar conditions a 3,500,000:1,450,000 or 2.5:1 ratio. Considering the 20-degree angle specimens the ratio is 775,000:525,000 or about a 1.5:1 ratio. These additional points transplanted from Fig. 19 to our graph are shown

as darkened points to differentiate from the authors' original curve data. The added points do not affect the general slope direction of the authors' curves.

However, the points were added to suggest a possibility. It has been shown that there exists in the authors' results variations in endurance life of 2.5:1 for similar testing conditions. Now let us take the 80-pound blast pressure, 90-degree angle point in Fig. 18 which is causing the reversal of curvature. Let us assume that the same variation in fatigue life exists in specimens tested under these conditions. From Fig. 18 the life of this specimen at a nominal stress of 45,000 pounds per square inch was 700,000. Applying the 2.5:1 ratio and the possibility of having a specimen endure 2.5 x 700,000 or 1,750,000 cycles is not beyond reasonable conception. If this new value were plotted on the proper curve in Fig. 18 the 80-pound curve would suffer no reverse in curvature. This possibility is indicated by a darkened point on our graph. It is not known, of course, that this variation does exist in a 90-degree angle of blast with 80-pound pressure of blast but it has been shown that that variation did exist in the 90-degree angle specimens using 65-pound pressure blast. By this data, it is being indicated that if the curves were established in Figs. 17 and 18 by single test values that the reversal of curvature must be accepted with complete reservations until amplifying results are available.

The reversal of curvature must be also questioned from another angle. Quoting the authors: "The data seem to indicate that the degree of cold work and the severity of the notches, as shown in Figs. 27, 28 and 29, both increase with angle and pressure of blast." It is admitted that the cold work degree would increase with the angle and pressure of blast. However, it does not appear from Figs. 27, 28 and 29 that the severity of the notches increases with angle and pressure of blast. Examining Figs. 27 and 28 it will be seen that the notch effect caused by the 65-pound pressure is more pronounced than the notch effect caused by the 35-pound pressure blasting. The increase in notch concentration probably explains the relative positions of the 35-pound and 65-pound curves in Fig. 17. However, the notch effect of the 65-pound pressure blasting is decidedly worse than the notching effect caused by the 80-pound blast pressure. Thus it cannot be concluded that the severity of notches increases with the pressure of blast. Likewise if any of the three Figs. is examined it will be found that the 90-degree angle of blast specimen always has the largest radius of curvature at the base of its notches. Thus it cannot be concluded that the severity of the notches increases with the angle of blast.

Examining again Fig. 29 it will be seen that the radii at the bases of the notches in the 90-degree specimen are very generous in comparison with the 75-degree specimen. Likewise the cold work effects are greater with the 90-degree specimen than with the 75-degree specimen. Yet the endurance life of the 90-degree specimen is only fifty per cent of the endurance life of the 75-degree angle specimen when subjected to a fatiguing stress of 45,000 pounds per square inch. The facts do not seem to support the theory and again indicate that the reversal of curvature in the 80-pound curve of Fig. 18 is highly questionable.

This discussion is offered only as another interpretation of the data offered by the authors. It is presented only as constructive criticism. The reward of an investigator lies only in that his work awakens interest in fellow investigators. It has been a pleasure to offer this discussion.

Oral Discussion

W. J. MERTEN:[1] I would like to ask the speaker whether or not the warping of the specimens he blasted indicated that the irregularity of blasting was such that he actually introduced localized strains, which may have been due to irregularities of structural conditions of the specimens in addition to any differences in the intensity of impingement of blasting particles. The attack of the problem and the results of the work are of considerable interest to roll makers, since surface conditioning and finishing by methods other than grinding is of great help for the production of special surface finishes on strip and sheet.

Authors' Closure

We appreciate the interest shown in our paper and the discussion submitted by Messrs. Merten, Bloxdorf, and Harvey.

Inasmuch as Mr. Frye has been abroad since the presentation of this paper, the discussion to follow in no way expresses his opinions or beliefs in the questions involved.

Regarding Mr. Merten's question as to the warping of the blasted specimens, we found that in sand blasting, as carefully as the conditions of blasting were controlled, a number of specimens in each group were warped after blasting. Undoubtedly, the warping was caused by localized stresses either being set up or released in the specimen by the blasting, but in just what manner they were introduced or released I cannot say. I would hasten to add that any warped specimens were discarded and not used in our investigation.

Relative to Mr. Bloxdorf's interest in the fatigue machine used in this investigation, I would like to say it is my understanding that in the near future a paper will be published by the designers giving full details of construction and operation.

Mr. Bloxdorf has suggested an ingenious hypothesis for explaining premature failure of specimens by the introduction of such amounts of cold work at the line of contact between the specimen and grip rolls that actual embrittlement of the surface took place. Early in our investigation we made superficial hardness tests at the line of contact on specimens that did not fail. We found no apparent increase in hardness. Hence we believe no embrittlement of the surface took place.

Regarding Mr. Bloxdorf's question about the pickling procedure used, no inhibitors were employed in the pickling bath and the ferrous sulphate content of the solution was not known.

Mr. Bloxdorf's question regarding the surface condition before and after pickling is interesting.

Edges of specimens both with the scale intact and after removal of the scale by acid pickling were examined microscopically. The surface of the metal adjacent to the scale was relatively smooth in unpickled specimens as compared to the acid pickled surface. Consequently we believed that the relatively rough and notched surface in Fig. 13 was due to the acid attack in the pickling process and not due to the mechanism of scale formation.

[1] Metallurgical engineer, Pittsburgh Rolls Corp., Pittsburgh.

We did not determine what was the maximum surface hardness obtainable by blasting. We did, however, have groups of specimens blasted with a relatively large round steel shot (No. 6 and 10) at 80 pounds per square inch pressure and found that the resulting superficial hardness was N15-74. We believe that this high hardness number obtained is a good example to illus-

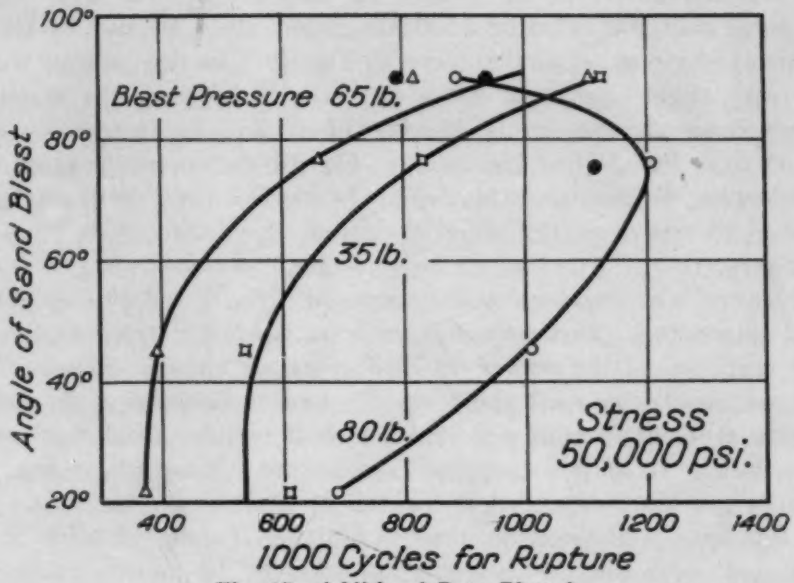


Fig. 17—Additional Data Plotted.

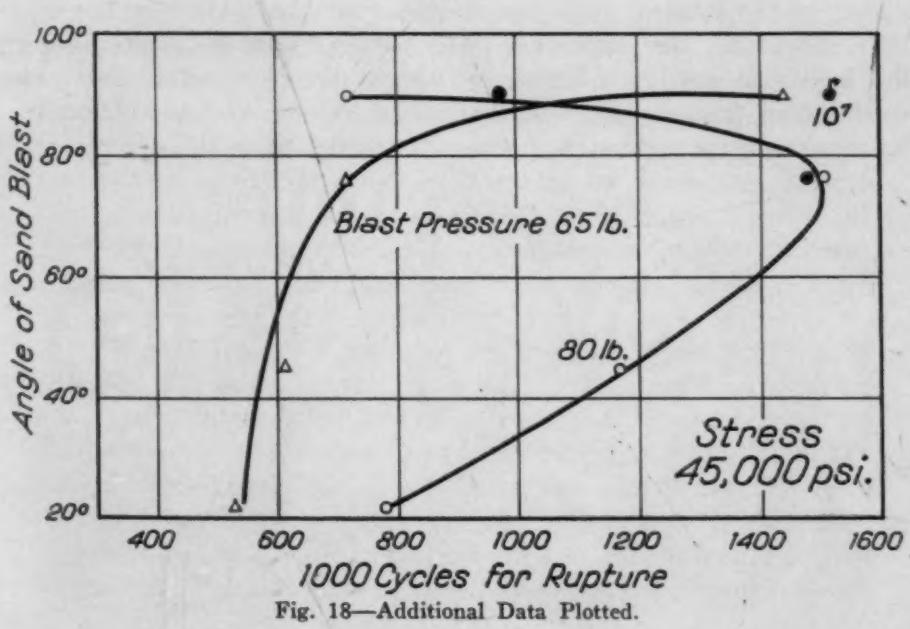


Fig. 18—Additional Data Plotted.

trate that the surface hardness can be increased to a considerable extent by the choice of proper blasting media (blasting pressure constant). These specimens were severely warped after blasting and could not be used in our fatigue machine.

Mr. Harvey's extrapolated curves between 0 and 20 degrees blasting angle lead to some interesting speculation. We should not, of course, be willing to place much reliance on such extrapolation without having actual test data available, however interesting they may appear.

Regarding Mr. Harvey's selection of points on the stress-cycle curve of Fig. 19 and the difference he finds when comparing them with Fig. 18, it will be noted that the value of 3,500,000 cycles which he uses is taken from the relatively flat portion of the curve in Fig. 19. In this part of the fatigue curve a very slight change in stress or a slight defect in the specimen will cause very large changes in the number of cycles. In fact, if the 1,450,000 cycle point from Fig. 18 had been used in Fig. 19, the curve would change very little. Likewise, for specimens blasted at 20 degrees, little or no change would be found in the curve in Fig. 19 if the value of 525,000 cycles from Fig. 18 had been used.

Mr. Harvey's suggestion that the curves in Figs. 17 and 18 may not reverse is indeed interesting. However, further tests conducted since that time confirm the reversion of the curves at 75 degrees, as already shown. The data obtained are plotted in solid points on the two accompanying sets of curves. At a stress of 45,000 pounds per square inch it will be noted that one of the specimens ran to 10 million cycles without failure. Inasmuch as this stress is 2500 pounds per square inch below the fatigue limit of the material in the as-received condition, and since variation in blasting is quite probable, it may be expected that some specimens would continue to 10 million cycles without failure. The preponderance of 5 out of 6 points which lie on the original curves indicates, in our opinion, quite conclusively that the curves do reverse.

We should not like to dispute Mr. Harvey's opinion about the intensity of the individual notches. Rather we should prefer to allow the reader to devise his own explanation about the fatigue results we have obtained. The explanation we have suggested in the text seemed to us the most logical one.

ELECTROMAGNETIC MEASUREMENTS AND STEEL STRUCTURES CORRELATED

By Carl Kinsley

Abstract

Nondestructive tests are made, by electromagnetic measurements with a dynamometer and subsidiary phase shifting transformers, of the uniformity of steel samples or of the character and amount of their differences.

The preparation of the testing circuit for the reception of the sample to be tested is of critical importance. Before a sample has been treated so as to change its structure, it is placed in the magnetizing coil and the electromotive force induced in the testing circuit is measured with respect to an empty coil—an air core.

This initial electromotive force is completely balanced by introducing into the circuit an equal, but opposing, electromotive force. This is synthesized from the electromotive force derived from any convenient piece of steel supplemented by phase shifting transformers which term by term neutralize the induced electromotive force. The opposing electromotive force is called the "balancing wave" and it has an opposite sign with respect to the corresponding induced electromotive force.

Each sample is now treated so as to change its structure. It is then placed in the magnetizing coil and the value of the additional electromotive force resulting from the treatment is obtained as a series of harmonic terms. The amplitude and phase angle of each of the significant terms of the complete wave is evaluated and their interpretation gives the character and the amount of the change produced in the steel sample.

Illustrations are given of the metallurgical differences between the samples and between the different sections of the same sample, also of the effect of different tempering temperatures on similar samples which had been quenched alike. The significance of different phase angles with similar electromotive force waves is illustrated with superimposed curves. The relation of the phase angle to the character of the change in the steel structure is pointed out.

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. The author, Carl Kinsley, is consulting engineer, 32 West 40th St., New York City. Manuscript received June 23, 1937.

Outline of the Method of Testing

Theory

ITS hysteresis loop is assumed to be a unique characterization of any specimen of steel with respect to its chemical analysis, metallurgical state, physical condition and material homogeneity.

An induced electromotive force is developed in a testing circuit when the specimen is placed in its magnetizing coil through which passes a simple sine wave of alternating current. No change in the hysteresis loop can occur without causing a corresponding change in the electromotive force.[1]

The method of measurement is described below which makes possible the correct interpretation of the electromotive force in terms of the characteristics of the steel specimen.

(1) A list of the apparatus employed follows:

Dynamometer—a sensitive instrument for laboratory use, relatively insensitive for mill use.

Ammeters—for exact laboratory work but not used during mill operations.

Phase shifting transformers—converted selsyn motors can be used for all purposes.

Circuit controlling rheostats and switches which are used in laboratory work and for making the preliminary adjustments for mill operations.

(2)—A schematic drawing of the apparatus and the circuits employed in the application of the method of testing described in this paper is given in Fig. 1.[2] This shows the use of duplicate coils in the testing circuit. They are connected in a bridge with noninductive resistances so that each arm has approximately the same impedance. The bridge is a part of the magnetizing circuit which is designed to supply the same ampere turns per centimeter employed in the remainder of the magnetizing coils.

If one of the magnetizing coils is left unoccupied—an air core—and a specimen is placed in the other, the electromotive force in the testing circuit will be exactly the same as that given by a single

[1] C. W. Burroughs, *Proceedings*, American Society for Testing Materials, Vol. 13, 1913, p. 571.
S. R. Williams, Transactions, American Society for Steel Treating, Vol. 11, 1927, p. 677.
Thomas Spooner, *Proceedings*, American Society for Testing Materials, Vol. 26, Pt. II, 1926, p. 116.

[2] British Patent No. 336.987, 1930.
The Industrial World, (London) Vol. 22, No. 131, 1932, p. 9.

testing coil which has no electrical connection to the magnetizing circuit. Apparatus and circuits simplified in this way are sometimes found to have a considerable advantage.

(3)—The method of testing is used effectively with both a single coil in an independent testing circuit and duplicate coils connected in

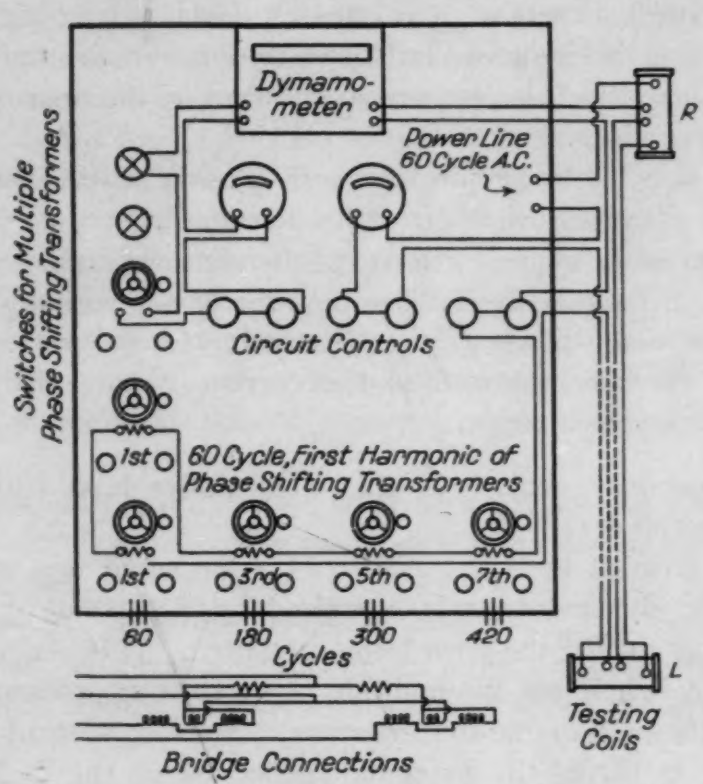


Fig. 1—Balancing Wave Method of Nondestructive Testing.

a bridge and forming a part of the magnetizing circuit. The method has been previously described[3] but will be outlined here and applied to particular problems.

There are three steps to be taken of which two pertain to the gathering of the information needed and the third to its interpretation.

First—The complex electromotive force derived from the hysteresis loop is analyzed into its simple harmonic components by the apparatus. This gives the constants of the terms in the Fourier's series, into which any periodic function can be resolved.[4]

$$(3)\quad e = V_1 \sin(\omega t - \phi_1) + V_3 \sin(3\omega t - \phi_3) + \cdots + V_n \sin(n\omega t - \phi_n)$$

[3]U. S. Patents 1,743,087 (1930) and 1,910,770 (1933).
Carl Kinsley, *Proceedings*, American Society for Testing Materials, Vol. 37, June 1937.
[4]J. W. Mellor, "Higher Mathematics," (1906), Chapter VIII.

The odd terms are alone needed when the positive and negative portions of the E.M.F. curve are similar.

(4) $i = I \sin (\omega t - \phi)$ This is used as the reference vector and is plotted parallel to the X axis so that its phase angle is zero, $\phi = O$

or

$i = I \sin \omega t$

e = the induced electromotive force in the testing circuit which is obtained as the sum of the instrument readings.

v_n = the maximum values of the sine wave. The subscript gives the order of the harmonic.

ω = the angular velocity of the vector in radians per second or $\omega = 2\pi/T$. T = the time of one period.

ϕ_n = the phase of the electromotive force vector which is here referred to the current vector, placed at zero phase angle.

The harmonic analysis of the electromotive force curves is carried out as follows:

Each term of the harmonic series is measured separately. The field of the dynamometer is energized by a current of the same frequency as that of the term being measured. This is done through the selector switch and the multiple phase shifting transformer connected to the field of the dynamometer. Set the phase of the transformer so as to get the maximum deflection of the dynamometer. The dial of the transformer then gives the value of the phase, ϕ_n, and the dynamometer deflection is proportional to the maximum value of the electromotive force of the harmonic term in volts, V_n.

Second—Electromagnetic measurements in nondestructive testing should be made with accuracy since relatively small changes in analysis and structure of the steel specimen often indicate important changes in quality. Errors in measurement can be avoided only when the starting point is fixed by using a completely neutral circuit —the zero.

Any circuit containing an electromotive force can be brought to zero by introducing a balancing wave which term by term completely neutralizes each sine wave of the Fourier's sine wave series representing the electromotive force originally present. The balancing wave, therefore, is of fundamental importance in obtaining the correct measurement of any additional electromotive force which results

from any change in the steel specimen or in determining the differences between successive samples.

Third—The interpretation of the electromagnetic measurements rests on the correlation between the additional electromotive force and the known changes in the steel sample.

The purpose for which the steel is to be used and the degree of perfection required must be known in order to decide what initial information is needed in regard to the sample of steel which is used in establishing the zero. This is pointed out specifically in connection with the illustrations given in the graph of Fig. 4.

The electromagnetic measurements furnish the phase and amplitude of each significant term of the harmonic series of the electromotive force. Each of the above constants is affected by the maximum value of the current used in the tests. It has been found possible to interpret correctly complex differences between specimens by the use of the measurements obtained accurately under controlled conditions.

In commercial work carried on at high speeds—e.g., 100 feet per minute—a differentiation was made with one instrument between a number of factors. For instance, the location of seams or cracks in the presence of large differences in cold work was carried on in operating mill inspection. Subsequent critical examination of the material, both rejected and passed, did not disclose any errors in the results of the nondestructive tests.

Application of Balancing Wave Method of Testing

Location and Measurement of Decarburization

Considerable difficulty was experienced from the presence of intermittent decarburization in steel wire of the following specification.

No. 10 stock was used finished to the dimensions of 0.55 centimeter by 0.51 centimeter. The wire was cold drawn and was annealed twice during the reduction. After the final anneal it was given two finishing passes.

The mill test for decarburization is to harden both ends of each bundle by immersing in lead at about 1550 degrees Fahr. (845 degrees Cent.) and quenching in oil at room temperature. Each hardened end is tested with a file.

It is found that the decarburization of the finished wire is intermittent, or spotty, as the result of drawing after it had been decarburized. When graded in accordance with the mill tests it is found that frequently bundles of wire are "accepted" which are badly

Chemical Analysis

	Per Cent
Carbon	0.51 to 0.55
Manganese	0.55 to 0.75
Silicon	0.11 to 0.14
Sulphur	0.50 to 0.05
Phosphorus	0.05 as maximum.

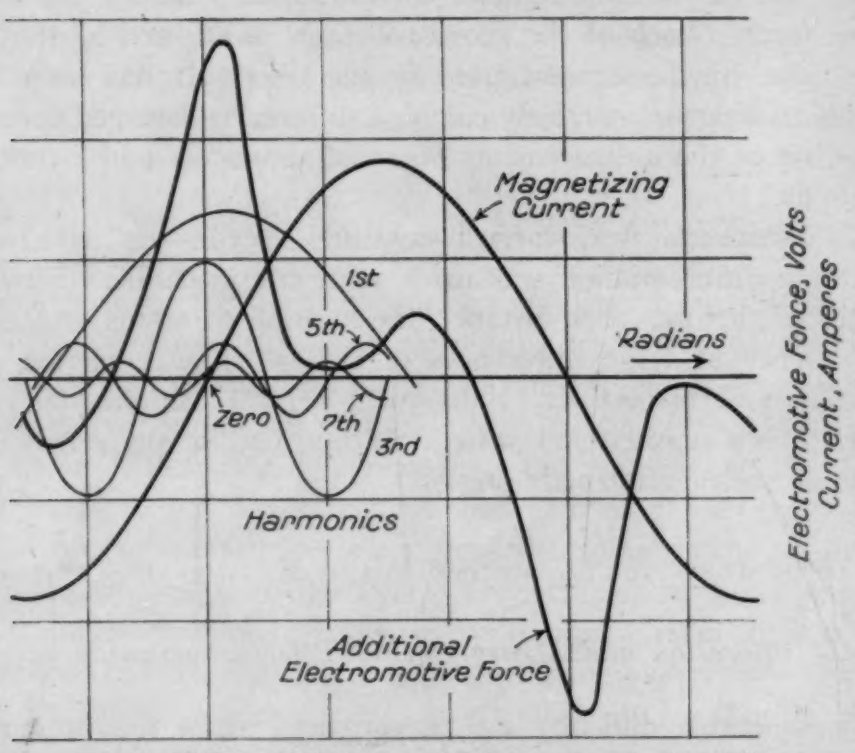


Fig. 2—Method of Testing as Applied to Decarburized Wire.

decarburized inside of the ends which had been tested and, conversely, bundles of wire are rejected which are nearly free of decarburization.

In Fig. 2 is given an illustration of the method of testing as applied to decarburized wire. From the bundles which had been given the mill inspection a sample was chosen, which the electromagnetic tests showed was entirely free from decarburization. (It came from a bundle which had been rejected.) The sample was marked A.

Another piece was taken from a bundle (accepted as free from decarburization by mill inspectors) and two places were chosen which differed in the amount of the decarburization shown by the non-destructive tests. The place which had the least decarburization was marked B and the one with considerable decarburization was marked C.

The testing procedure was as follows:

Sample A was placed in coil R. Its measurement with respect to air (coil L unoccupied) was not taken, as the base metal was not of importance.

Sample B was placed in coil L and as there was some base metal difference it was largely eliminated by introducing as a balancing wave an opposing electromotive force of the first harmonic alone having the value $e_{bw} = -38.5 \sin (\omega t - 32°)$. The phase of $-32°$ indicated that there was probably a difference in the annealing of A and B as shown in previous work. The remaining harmonics gave a slight peak at the phase which indicates decarburization of negligible amount.

The samples B and C were only 4 feet 9 inches (four feet and nine inches) apart and had the same base metal. Sample C was now used to replace sample B and the balancing wave was unchanged. The electromotive force equation of sample C then gave the difference between sample C and sample B, as follows:

$$(5) \quad e_e = +62.2 \sin (\omega t - 77°) - 43.5 \sin (3\omega t + 90°) - \\ - 13.7 \sin (5\omega t + 139°) - 7.5 (7\omega t + 153°)$$

The higher harmonics have relatively large amplitudes. Their phase values cause them to combine to produce the characteristic peak at the correct phase angle. (See Fig. 5 also.)

In order to make it easily visualized the electromotive force equation of the above sample C has been synthesized from the separate harmonic terms in Fig. 2 for one half of the wave.

The analysis of this result shows that the ferrite surface of the specimen has been magnetically saturated at a relatively low current value so that from a phase angle of about 30 to 120 degrees of the current curve (the upper half of the current value) the ferrite plays no part in the electromotive force curve which within this range is due to base metal differences, here apparently negligible. A decrease in current amplitude causes the electromotive force curve to become wider, decreases the phase angle but does not materially reduce its

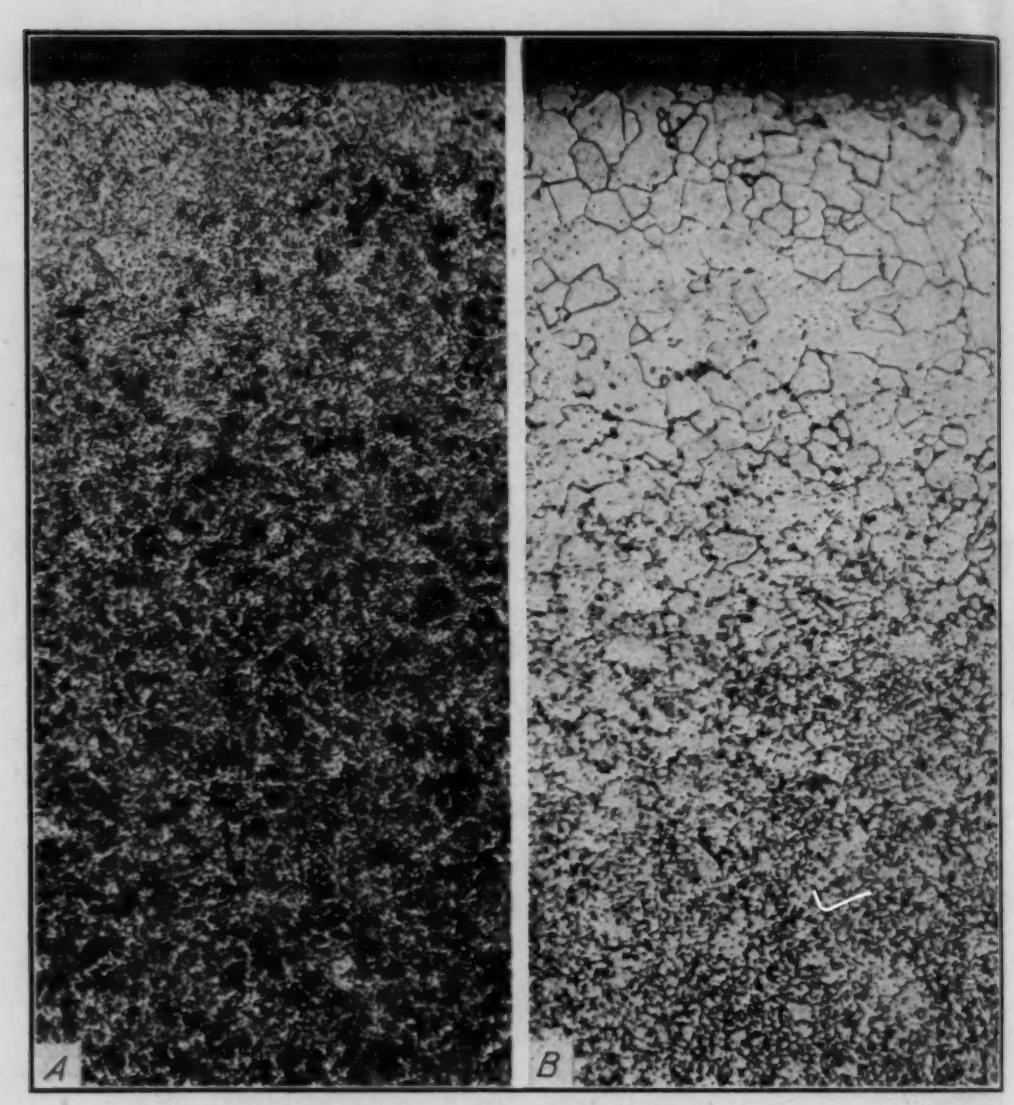


Fig. 3—Structure of Specimens B and C. × 200.
A—Depth of Decarburization of Specimen B—0.001 Inch.
B—Depth of Decarburization of Specimen C—0.010 Inch.

height. An increase in the current maximum causes the electromotive force peak to become more narrow, increases the phase angle and does not greatly increase its height even with a current of doubled value, since the ferrite was already saturated.

The narrowed peak, however, requires a redistribution of the relative values of the harmonics. The harmonics up to the eleventh or even higher may have appreciable amplitudes. With a standardized procedure it is easily possible to draw a calibration curve which will give the depth of decarburization from the value of one of the harmonic terms with an accuracy to 0.0005 inch.

Fig. 3 shows the structure of the specimens B and C. Specimen A was not photomicrographed but was etched and examined and found to be free from decarburization. Another specimen, D, was estimated from the electromotive force measurements to be similar to B in regard to the slight amount of decarburization present. It was photomicrographed and its structure was found to be the same.

Report of Examination by Microscope

Specimen A—Less decarburization than specimen B. (Not photomicrographed)

Specimen B—Very slight carbon decrease at every surface, 0.001 inch.

Specimen C—Decarburized on all four surfaces to depth of approximately 0.010 inch. General structure is spheroidized carbide. Decarburized zone structure is ferrite and some interstitial carbide.

Specimen D—Similar to specimen B.

Structural Changes Due to Tempering

Many problems involving the structure of steel specimens can be solved by the use of the balancing wave method of testing. The application to quenched and tempered rods is given as an illustration.

The rods used in this investigation were cold drawn and centerless ground to 0.18 inch diameter. They were not annealed or normalized. All were quenched at 1610 degrees Fahr. (870 degrees Cent.) in oil at 67 degrees Fahr. (25 degrees Cent.) to 85 degrees Fahr. (35 degrees Cent.). They were then tempered by a standardized practice at temperatures between 930 degrees Fahr. (500 degrees Cent.) and 1290 degrees Fahr. (700 degrees Cent.)

Chemical Analysis

	Per Cent
Carbon	0.85
Manganese	0.35
Silicon	0.17
Phosphorus	0.035
Sulphur	0.034

Metallurgical Report

All the samples were etched in a 1 per cent nitric acid solution in alcohol. They were examined under an oil immersion lens at about X 2000 diameters.

Specimen S tempered at 930 degrees Fahr. (500 degrees Cent.)
Specimen V tempered at 1020 degrees Fahr. (550 degrees Cent.)
Specimen Z tempered at 1110 degrees Fahr. (600 degrees Cent.)
Specimen X tempered at 1290 degrees Fahr. (700 degrees Cent.)

There was a progressively changing structure from specimens S to V to Z to X. Specimen S, tempered at 930 degrees Fahr. (500 degrees Cent.) showed carbide particles resolved and beginning to indicate the pattern of the martensite crystals.

Specimen X, tempered at 1290 degrees Fahr. (700 degrees Cent.) showed spheroidized carbides becoming well distributed and blurring the outline of the martensite structure.

These specimens covered the range of tempering temperatures within which a steel structure could be resolved by the microscope. The electromagnetic measurements, however, give a continuous curve far beyond the point where the microscope can follow. Physical tests give results which indicate structural changes in the steel so that it is a reasonable assumption that the changing values from electromagnetic measurements are caused by changes in the steel structure.

Only the fundamental, the first harmonic, is needed for the investigation of the structural changes caused by the above different tempering temperatures.

The symbolic method of writing the equations can then be used and combined with the polar co-ordinate method of plotting the results.[5]

$$(6) \qquad E = I\ (r - jx) \text{ and } \phi = \tan^{-1}\ (-x/r)$$

E = virtual value of electromotive force.
I = virtual value of current.
BW = balancing wave which neutralizes the electromotive force.
r = equivalent resistance of circuit.
x = reactance of circuit.
ϕ = phase of electromotive force with respect to the current as reference vector.
n = A subscript referring to a particular electromotive force derived from the specimens indicated.

Fig. 4 is a graph showing the electromotive force values. They are measured from any convenient zero but can be referred back to the fundamental condition of an air core. The procedure is as follows:

A piece of steel of any size or analysis is chosen, such as specimen O, on the basis that it induces in the circuit a value of electromotive force conveniently close to the E.M.F. due to the specimens.

[5] C. P. Steinmetz, "Alternating Current Phenomena," (1916) Chapter V and VIII.

It is placed in one of the coils and the other coil is left open. The electromotive force is E_o having an amplitude of 23.8 and a phase angle of 105 degrees. This is plotted from a zero chosen on the graph as the location of Specimen O. When another piece of steel,

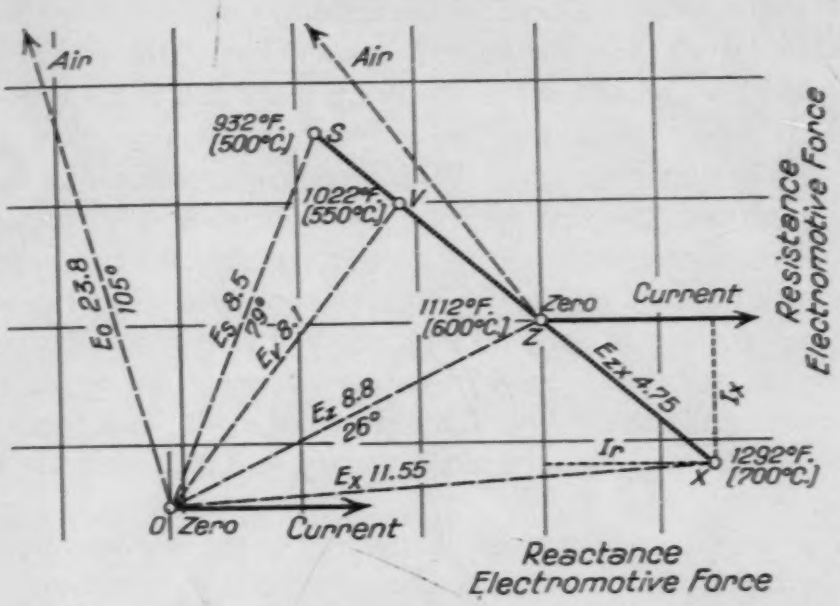


Fig. 4—Electromotive Force Measurements of Rods Quenched and Tempered. Data Plotted in Polar Co-ordinates.

Z, is placed in the second magnetizing coil the electromotive force is changed to E_z which represents the difference between the specimen O and the specimen Z.

The electromotive force, E_z, is equal to 8.8 at the phase angle of 26 degrees. Specimen Z with respect to air has an electromotive force of the following vector value:

$$E_{zz} = E_o + E_z \text{ or } E_{zz} - E_o = E_z \tag{7}$$

A balancing wave can be introduced into the bridge circuit with the dynamometer which will neutralize E_z so that the dynamometer will be exactly at zero for all phase values of its field current

$$E_z - BW_z = 0. \tag{8}$$

This in effect transfers the zero from the magnetizing coil having an air core to the magnetizing coil with specimen Z as the core.

Substitute now another specimen X for specimen Z and another electromotive force will appear,

$$E_{zx} = E_z - BW_z \tag{9}$$

having the value of 4.75 and the phase angle — 41 degrees. This

vector is the "additional electromotive force" used in the correlation of the results of the measurements with the change in the steel.

The resistance electromotive force, Ir, and the reactance electromotive force, Ix, are obtained from E_{zz} as indicated on the graph.

These are the two most significant quantities associated with the hysteresis loop. Since the current is a sine wave, the energy loss in the material is proportional to its conductivity and to the area of the hysteresis loop. Moreover, the permeability is dependent on the shape of the hysteresis loop. With an advantageous choice of magnetizing current, the first term of the electromotive force series is the only term necessary for the correct correlation of the measurements with the steel differences between specimens of this group.

Small changes in the steel structure will give small electromotive force values and the accuracy of the measurement can be maintained by increasing the sensitivity of the dynamometer. This requires the zero to be accurately located along the phase angle significant of the change.

The omission of the higher harmonics of the electromotive force wave in the use of magnetic analysis methods is hazardous, unless preceded by an investigation of their relative importance. A still more serious hazard is the inaccurate measurement of the electromotive force due to an incorrect zero. The total omission from the measurements of the phase of the electromotive force with respect to the current vector limits the successful use of the magnetic analysis tests previously employed to very special cases.[6]

The measurements shown on the graph of Fig. 4 are capable of many combinations to meet the great variety of conditions found in both laboratory investigations and commercial work. This is of particular value in neutralizing the effect of undesirable factors. For instance the electromotive force vector, due to cold work, can be located in quadrature with the significant vector, and it will have no effect on the dynamometer.

The measurements from the zero given by the air core to the other zeros used in the progress of the work suggest surveying methods with its initial sea level datum mark and the subsequent bench marks from which the local measurements can be made with accuracy and the whole survey referred back to the starting point.

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[6] A. V. de Forest, *Proceedings*, American Society for Testing Materials, Vol. 23, Pt. II., 1923, p. 611.
A. V. de Forest, *Proceedings*, American Society for Testing Materials, Vol. 26, Pt. I., 1926, p. 742.

Importance of the Electromotive Force Phase

When the magnetizing current is a simple sine wave a distortion of the periodic curve of electromotive force is introduced by any hysteresis loop in which the magnetic flux is a complex function of the magnetizing force. This includes all ferrous magnetic materials. The value of the current at which the distortion of the electromotive force curve is most pronounced is a guide to determining the character of the steel. This results in two pronounced effects which can be made use of in interpreting the results of the measurements.

First—The amplitudes and phase values of the higher harmonics shift with every change in the steel so that they reinforce each other to produce the E.M.F. peaks at the correct phase position in each wave of the current. These relative amplitude and phase values can be used in interpreting the electromotive force curve which has been analyzed into the Fourier's series.

Second—The pronounced peaks also have a considerable first harmonic. This can be considered as a relative change in the value of the simple average reactance of the circuit due to the change in the permeability of the steel caused by the change in the structure.

There is also a change in the resistance of the circuit due principally to the change occurring in the steel structure which affects the energy losses.

If these changes do not occur in the same proportion then the phase angle of the first harmonic of the Fourier's series registers the irregularity.

It is found by experience that a characteristic change in the structure is accompanied by the appearance of a particular phase angle. If the change in the steel is just beginning to appear, the phase angle of the electromotive force will at once take the value which is characteristic of the new structure. The amplitude of the additional electromotive force, however, will be small. As the change progresses the phase angle remains constant but the amplitude of the fundamental term of the Fourier's series increases.

$$(10) \qquad V_1 = I\sqrt{r^2 + x^2} \text{ and } \cdot \phi = \tan^{-1}(-x/r)$$

With the character of the structure remaining the same, the constants, r and x, increase in value as the change in the steel structure progresses. The proportionality of x and r remain the same and, consequently, the phase angle remains unchanged while the

change in the steel structure causes a continued increase in the amplitude of the electromotive force wave.

This condition will not be recognized unless there is a perfect balance of the electromotive force in the circuit at the zero from which the measurements are made.

The *first* effect is made use of in interpreting the electromotive force curve which is characteristic of decarburization, as shown by Fig. 2 and equation (5).

The *second* effect is used in the analysis of the electromotive force values accompanying changes due to annealing.

Fig. 5 shows a superposition of the two curves in which the shape of the electromotive force curves are substantially the same but the

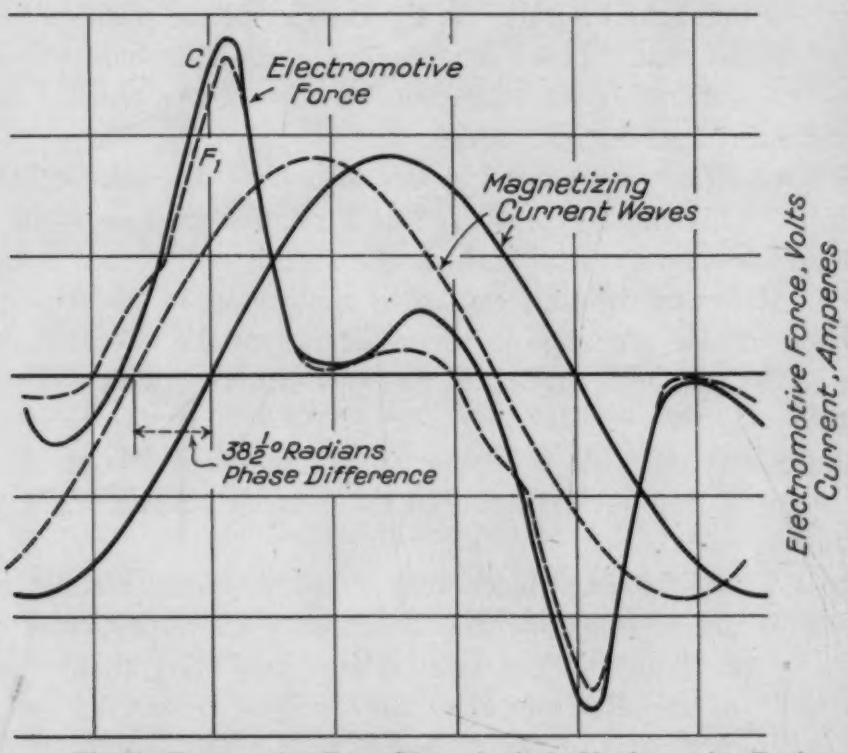

Fig. 5—Electromotive Force Phase Angle in Nondestructive Testing Work.

phase angles differ widely with reference to the peak values and, consequently, with reference to the phase value of the fundamental, or first harmonic, of the Fourier's series into which the two similar curves are resolved.

Specimen C, drawn in full line, is shown as synthesized from its harmonics in Fig. 2. Its electromotive force as analyzed by the testing apparatus into a harmonic series is given in equation (5).

Specimen F_1, drawn in broken line, is taken from another paper where specifications and details of the tests can be found.[7]

The equation of the harmonic function for specimen F_1 was obtained from the testing apparatus and synthesized into the curve plotted here. An oscillograph curve was also obtained and will be found as Fig. 2 in the above paper.

The equation is as follows:

$$(6)\quad e_n = 34.0 \sin(\omega t - 45°) + 18.7 \sin(3\omega t + 32°) - 8.1 \sin(5\omega t - 16°) - 4.0 \sin(7\omega t + 85°).$$

The approximate phase differences are given by the displacements of their respective magnetizing currents and taken from the graph as 38.5 degrees.

The practical importance of this analysis was shown in a striking manner on an extensive series of measurements in an operating mill. The balancing wave method of locating the zero and of using the phase angle as a guide to the cause of changes in the electromotive force values was employed. Flaws were located in 12½ per cent of the material by the tests which were carried out at 100 feet per minute. Subsequent metallurgical examination and physical inspection did not disclose any errors in the findings by the nondestructive tests, with one doubtful exception.

A commercial test under similar conditions made a little earlier by others in another mill, and reliably reported by one who took part in the tests—but not yet published—had the exactly opposite result of a 100 per cent failure; as shown by a careful metallurgical examination and physical inspection. The method of testing employed did not recognize the importance of the phase angle of the electromotive force and made no measurements of this essential factor for use in the interpretation of the results of electromagnetic measurements.

Conclusions

Representative tests are given of structural changes in steel specimens by decarburization and heat treatment, and the procedure for their identification by the balancing wave method of measurement is fully discussed.

The investigations from which these illustrations are drawn did not disclose any exception to the fundamental assumption of magnetic

[7] *Proceedings*, American Society for Testing Materials, Vol. 37, June 1937, Pt. I.

analysis as to the unique characterization of steel material by its hysteresis loop.

A further illustration is given of the importance of the phase angle of the electromotive force in interpreting the results of the measurements. The balancing wave method employed refers the characteristic equations of steel specimens to the air core as the initial zero, which ties together all electromagnetic measurements of every type of steel.

DISCUSSION

Written Discussion: By W. R. Ham, Head of Department of Physics, Pennsylvania State College, State College, Pa.

For a number of years I have been interested in the electromagnetic testing methods developed by Mr. Kinsley, not so much from the standpoint of usefulness in production inspection, as on account of the possibilities the method seems to possess for investigations of transitions in iron or nickel at elevated temperatures.

The large number of measurable variables available seems to be a distinct advantage, and in general, the method seemed so satisfactory that we are now starting to use a method similar in principle, but somewhat modified from an experimental standpoint, in the Physics Department at The Pennsylvania State College, as a check of results on transition phenomena in iron and nickel that we have recently been observing with pressure, temperature and time, by variation of rate of hydrogen diffusion.

My impression is that this obviously powerful method of analysis should be seriously investigated as to its possible use in connection with problems involving materials that are not ferromagnetic.

Written Discussion: By Wheeler P. Davey, Department of Physics, The Pennsylvania State College, State College, Pa.

Mr. Kinsley obviously has a very powerful method for investigating variations in the physical structure of ferromagnetic materials. His method is essentially a scheme for making, by electromagnetic methods, a Fourier Analysis of the electromotive force in the secondary of a transformer whose core is the specimen to be examined.

I am wondering whether it might be possible to make analogous Fourier Analyses of high frequency currents in air transformers in which the specimen would affect the shape of the electromotive force induced in the secondary winding. If so, the field of testing could be made to include nonferrous as well as ferrous material.

I should like to ask Mr. Kinsley whether he feels that the effects of such a tertiary on the induced current in a secondary winding could be made strong enough to give an acceptable sensitivity if the frequency were made quite high.

Author's Reply

The use of higher harmonics has been found to be necessary for many problems besides the one of decarburization used in this paper as an illustra-

tion. This method of testing has also been used in determining the depth of case hardening and there are many other purposes for which the higher harmonics are of importance. It has been proved, however, by many extensive experiments that for some purposes the fundamental harmonic of the testing current can be used alone as a sufficient guide. If the operator has demonstrated this fact for his particular tests, then it may be permissible to make use of only the fundamental, and that has been found to be a very simple method to employ in many commercial operations. It was suggested by Professor Ham that possibly some method of harmonic analysis following the usual form might be of advantage rather than this electrical method of making the harmonic analysis. The advantage in using the electrical method is that an exactly correct value of the amplitude and phase of each harmonic is obtained, while, the oscillograph curve is used with which to make the analysis in the usual form, it is necessary to take the amplitude of the elements from the oscillograph wave at particular places, put them into the equations and compute from them the values of the harmonics. This procedure introduces immediately a very large error in the factors employed in making the harmonic analysis that is not present in the case of the electrical analysis, because the constants of each of the harmonic terms are independently correct and they are immediately confirmed by introducing into the circuit a synthesized balancing wave which reduces the oscillograph figure to zero. Use may be made of any phase in the fixed coil of the instrument used in making the test and no matter how sensitive the instrument, it will still maintain its zero at all frequencies showing that all harmonics are balanced. Is it not then probably ten, or even one hundred, times more powerful in the analysis of a complex curve than such an analysis made by a computation where the amplitudes of the elements are taken from the oscillograph curve and thereby introduce, initially, a very large error? It also has the advantage of having the values of the harmonics obtained immediately, as they are needed in an experiment, without stopping to get them by using the method of computation. Consequently, not only are the exact values of the harmonics available but they can be recorded with the other data at once, and it takes only a moment to do so. It is necessary to balance only two things, the phase and the amplitude. Set the phase with reference to the magnetizing current so as to bring the instrument to zero, and then put the phase shifter in quadrature with its former position and change the amplitude of the balancing wave until it exactly neutralizes the electromotive force in the testing circuit and the instrument reads zero. There is no possibility of error since now a complete rotation of the phase shifting dial will cause no deflection of the instrument and the check is complete.

Professor Davey speaks of the possibility of using this method of testing for nonferrous materials. That has been done in trial experiments but there has been no particular problem in which a nonferrous material has been used and I have not made any extensive investigation. If it is considered that with this method it is easily possible to make the measurements to one tenth of one per cent of the whole quantity involved including the energy loss component of the impedance electromotive force, it is highly probable, consequently, that a nonferrous material will give an ample electromotive force for the measurement of the components needed for a complete analysis of the material

with respect to any structural change or the presence of a flaw. There is no theoretical objection and I have found no practical difficulty in using this method of testing for nonferrous materials. The advantage of high frequency currents would lie in differentiating between electromotive force changes when produced at different layers below the surface of the material. The higher the frequency of the magnetizing current the more effective is the limitation of the magnetic flux to layers close to the surface of the material. There would, consequently, be a different reaction in the testing circuit when the frequency of the magnetizing current was changed. If it was desired to make a single measurement to represent the whole of a cross section of uniform steel it would be better to use a low frequency. If, however, it was necessary to determine the depth below the surface at which a small seam occurred, then an additional measurement should be made with a higher frequency magnetizing current. The depth of the seam can be estimated from the phase which will be shifted from its normal value given by a surface seam while the deflection will indicate its size.

THE MECHANISM OF STEEL HARDENING AND TEMPERING AS INDICATED BY COERCIVE FORCE MEASUREMENTS

By R. S. Dean and Charles Y. Clayton

Abstract

Further confirmation is furnished of the lack of parallelism between magnetic and mechanical hardness in steels.

A hypothesis has been offered, which serves to explain the observed relation between hardness and coercive force in steels that have been subjected to various treatments. This postulates that one or more of four steps may take place in the hardening and drawing of steel, and cases are cited which show that certain steps may predominate under different conditions of treating.

Possible uses of coercive force as a shop-control method are suggested.

A DEFINITE lack of parallelism between mechanical and magnetic hardness as measured by coercive force in dispersion hardenable alloys was observed by one of the authors many years ago and has been repeatedly confirmed since.[1]

In such alloys as iron-molybdenum-cobalt the maximum of mechanical hardness is reached at a drawing temperature where the coercive force is actually a minimum. It may, therefore, be fairly assumed that mechanical and magnetic hardness arise from fundamentally different structural conditions in magnetic alloys, although both may be present in their maximum degree in certain alloys under the same conditions of treatment, as in ordinary steel.

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[1]R. S. Dean, U. S. Patent 1,904,859, 1933.
K. S. Seljesalter, and B. A. Rogers, "Magnetic and Mechanical Hardness of Dispersion Hardened Alloys, Transactions, American Society for Steel Treating, Vol. XIX, p. 553, 1932.
W. Köster, "Permanent Magnets on the Basis of Precipitation Hardening," *Stahl und Eisen*, Vol. 53, p. 849-856, 1933. Werner Jellinghaus Neue Legierungen mit hoher Koerzitivkraft *Zeit. Tech. Physik.* 70, p. 34, 1936.

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. Of the authors, R. S. Dean is Chief Engineer, Metallurgical Division, U. S. Bureau of Mines, and Charles Y. Clayton is Professor of Metallurgy, Missouri School of Mines and Metallurgy, and one of the consulting metallurgists, U. S. Bureau of Mines. Manuscript received June 21, 1937.

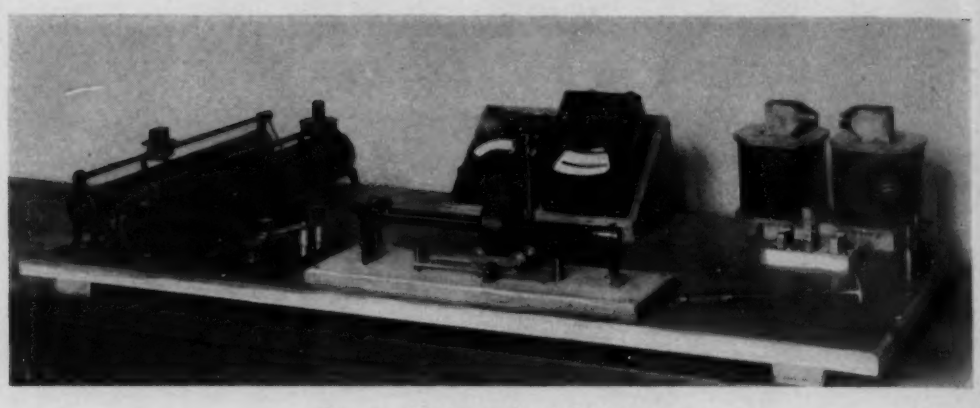

Fig. 1—Photograph of Instrument.

The structural conditions that make for maximum mechanical hardness in dispersion hardenable alloys, while not agreed upon in detail by metallurgists, may be broadly attributed to a keying of the planes of slip by the particles of the precipitating phase. Whether or not this keying action is purely mechanical need not concern us here.

On the other hand, the recent work of the Bureau of Mines[2] on

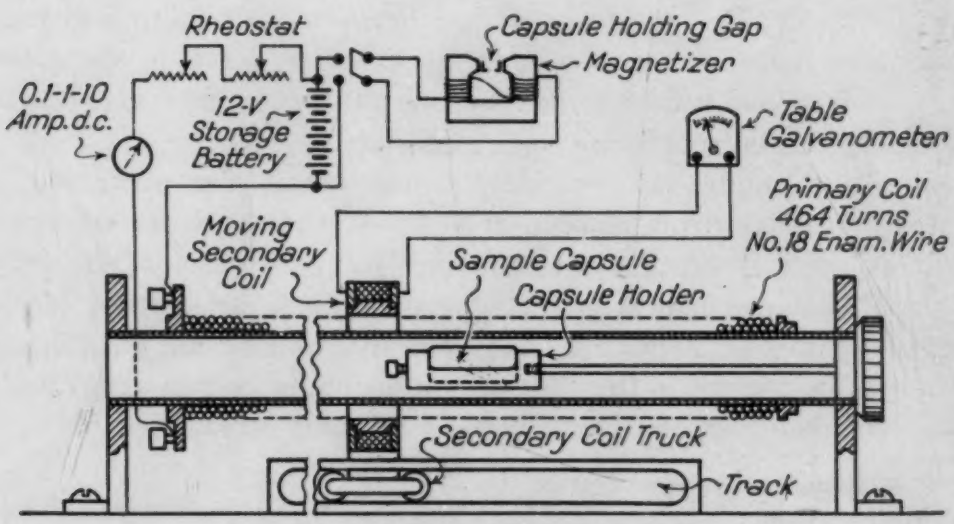

Fig. 2—Model 2 Coercimeter—Improved Form.

the magnetic properties of mineral powders has permitted the tentative conclusion that magnetic hardness is related to lattice discon-

[2]U. S. Bureau of Mines Report of Investigations 3223, Feb. 1934. Progress Reports—Metallurgical Division 1. Mineral Physics Studies.

U. S. Bureau of Mines Report of Investigations 3268, Feb. 1935, Progress Reports—Metallurgical Division 10. Mineral Physics Studies, p. 83, 91.

V. H. Gottschalk, "The Coercive Force of Magnetite Powders," *Physics*, Vol. 6, p. 127, 1935.

tinuities without regard to the existence of a second phase or any strains that might be set up by its formation or precipitation. These results have shown, for example, that with magnetite powder the coercive force is a linear function of the specific surface.

With these tentative generalizations as a guide to the interpretation, it seemed desirable to measure the variation of mechanical and magnetic hardness with heat treatment for a variety of steels. This was carried out by means of the coercimeter which is used in the Bureau of Mines work and has been described in detail elsewhere.[3] Fig. 1 is a photograph of the instrument and Fig. 2 is a diagram of the circuit. This instrument permits rapid and accurately reproducible determinations of magnetization coercive force which, if not of great absolute accuracy, are certainly comparative. The steel samples were all of uniform cylinders, ½ x 1 inch.

Relation between Grain Size and Coercive Force in Ingot Iron

As a test of the idea that coercive force could be taken as an approximately quantitative measure of the internal surface, ingot iron

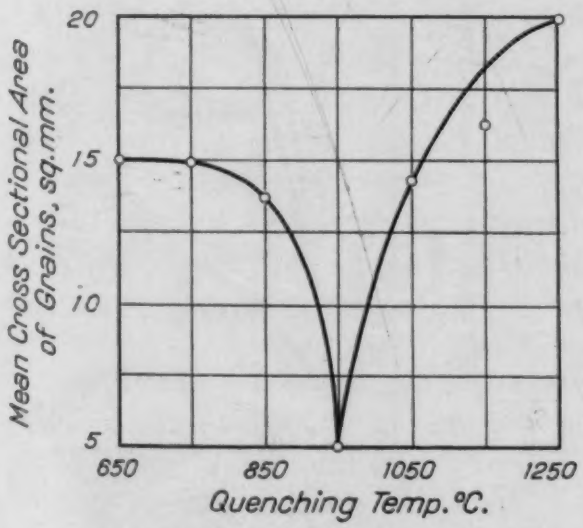

Fig. 3—Grain Size of Ingot Iron Quenched from Various Temperatures.

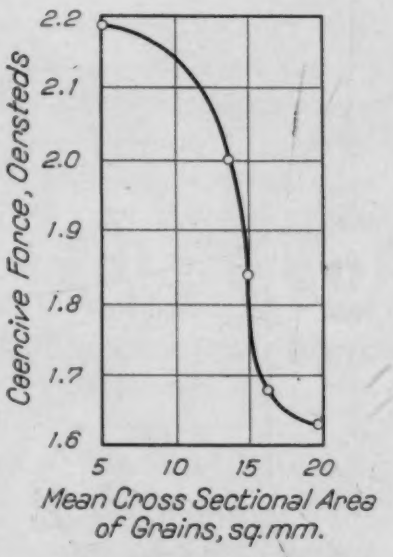

Fig. 4—Coercive Force of Ingot Iron as a Function of Grain Size.

having a wide variation of grain size was prepared by quenching from various temperatures. The results are shown in Figs. 3 and 4.

[3] "A Simple Coercimeter," *Mining and Metallurgy*, Vol. 17, May 1936, p. 261.
C. W. Davis and Max Hartenheim, "A Simple Method for the Determination of Magnetization Coercive Force." *Rev. of Sci. Instr.*, Vol. 7, Mar. 1936, p. 147-149.
U. S. Bureau of Mines Report of Investigations 3331, Progress Reports—Metallurgical Division 14. Annual Report of the Metallurgical Division, Fiscal Year, 1936.

It will be seen from Fig. 4 that the smaller the grain size the higher the coercive force, and if the data in Fig. 4 are replotted using $\frac{1}{\sqrt{\text{grain area}}}$—that is, internal surface instead of grain size—the approximately linear relationship in Fig. 5 is obtained.[4] By extrapolation this line goes nearly through the origin, indicating that the elements other than intergranular area which affect coercive force in this material are small.

Effect of Quenching Temperature on the Coercive Force of Plain Carbon Steels

Fig. 6 shows the effect of quenching temperatures on plain carbon steels. As would be expected, a temperature of 850 degrees Cent. gives the maximum coercive force in the carbon range 0.3 to 0.9 per

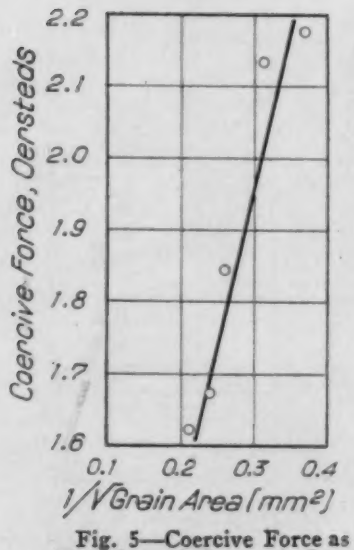

Fig. 5—Coercive Force as a Function of Internal Surface in Ingot Iron.

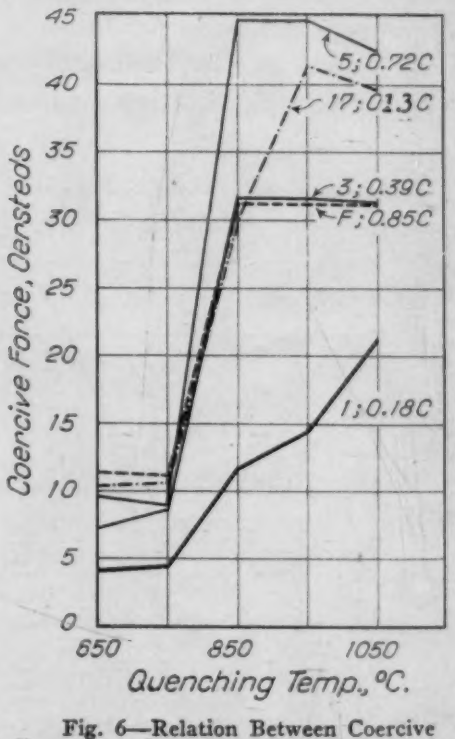

Fig. 6—Relation Between Coercive Force and Quenching Temperature of Plain Carbon Steels.

cent carbon since all of the carbon is in solution at this temperature. 1.3 per cent carbon steels require 950 degrees Cent. to give the maximum and steels with less than 0.2 per cent Cent. a still higher

[4] "Significance of Grain Surface Area," *Mining and Metallurgy*, May 1935, p. 228.

temperature. In view of these results a quenching temperature of 950 degrees Cent. was used in subsequent tests on steels in the composition range 0.2 to 1.37 degrees Cent.

Coercive Force and Rockwell Hardness of Plain Carbon Steels Quenched from 900 Degrees Cent. and Drawn at Various Temperatures

The following steels were used:

No.	Description	No.	Description
Y	0.16 C.	4	0.39 C. Coarse
ZX_2	0.19 C. Fine grained	QX_4	0.43 C. Fine
X	0.20 C.	ZX_2	0.44 C. Coarse
ZX_3	0.25 C. Coarse grained	5	0.72 C. Coarse
H	3120 Normalized	6	0.74 C. Coarse
HH	3120 Cold rolled	ZX_5	0.95 C. Coarse
B	1020 Normalized	F	0.95 C.
BB	1020 Cold rolled	ZX_6	0.97 C. Fine
3	0.37 C. Fine	17	1.30 C.

The results are shown in Figs. 7 and 8. Fig. 8, showing the hardness, indicates nothing unusual. Fig. 7 indicates that coercive force like hardness at first falls off gradually with increased drawing temperature, but with steels containing more than 0.3 per cent carbon there is a definite increase in coercive force for a drawing temperature of 500 degrees Cent. This increase in coercive force on drawing at 500 degrees Cent. in the case of 0.88 and 0.96 per cent carbon steel has been previously observed by Cheney.[5]

The obvious and probably correct interpretation of this unexpected increase is that austenite is retained by quenching and that such retained austenite does not break up until a temperature above 450 degrees Cent. is reached. But if this explanation is true why does the hardness continue its uniform fall throughout the drawing range? There seems only one conclusion to be drawn—that although decomposition of solid solution by quenching results in a parallel increase in hardness and coercive force, decomposition of the retained solid solution at 500 degrees Cent. results in an increase in coercive force but not of hardness. Solid-solution decomposition is therefore a complex process involving at least two kinds of structural changes, one of which affects coercive force and the other hardness. As an explanation of these results the following series of structural changes

[5] W. L. Cheney, "Preparation and Properties of Pure Iron Alloys II, Magnetic Properties of Iron-Carbon Alloys as affected by Heat Treatment and Carbon Content," Bureau of Standards Scientific Paper 463, Vol. 18, 1922-23, p. 609-636.

is postulated for the separation of a second phase from a solid solution.

1. *Internal surface is formed causing an increase in coercive force.* The solvent metal lattice being distorted by the atoms

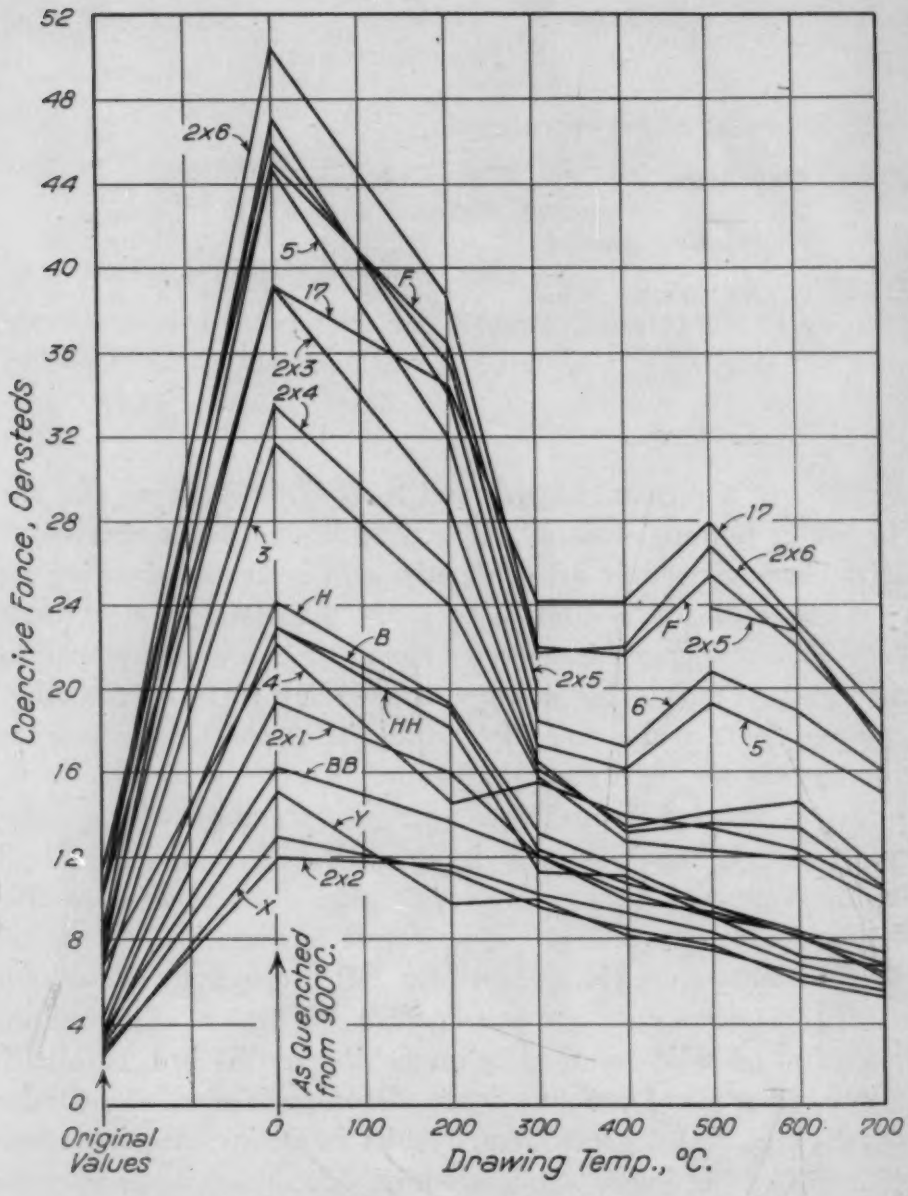

Fig. 7—Coercive Force of all Steels Tested as a Function of Drawing Temperatures.

of the solute breaks up into blocks some of which may be in compression, some tension, but the overall stress is below the elastic limit of the material. This step may be identified as the

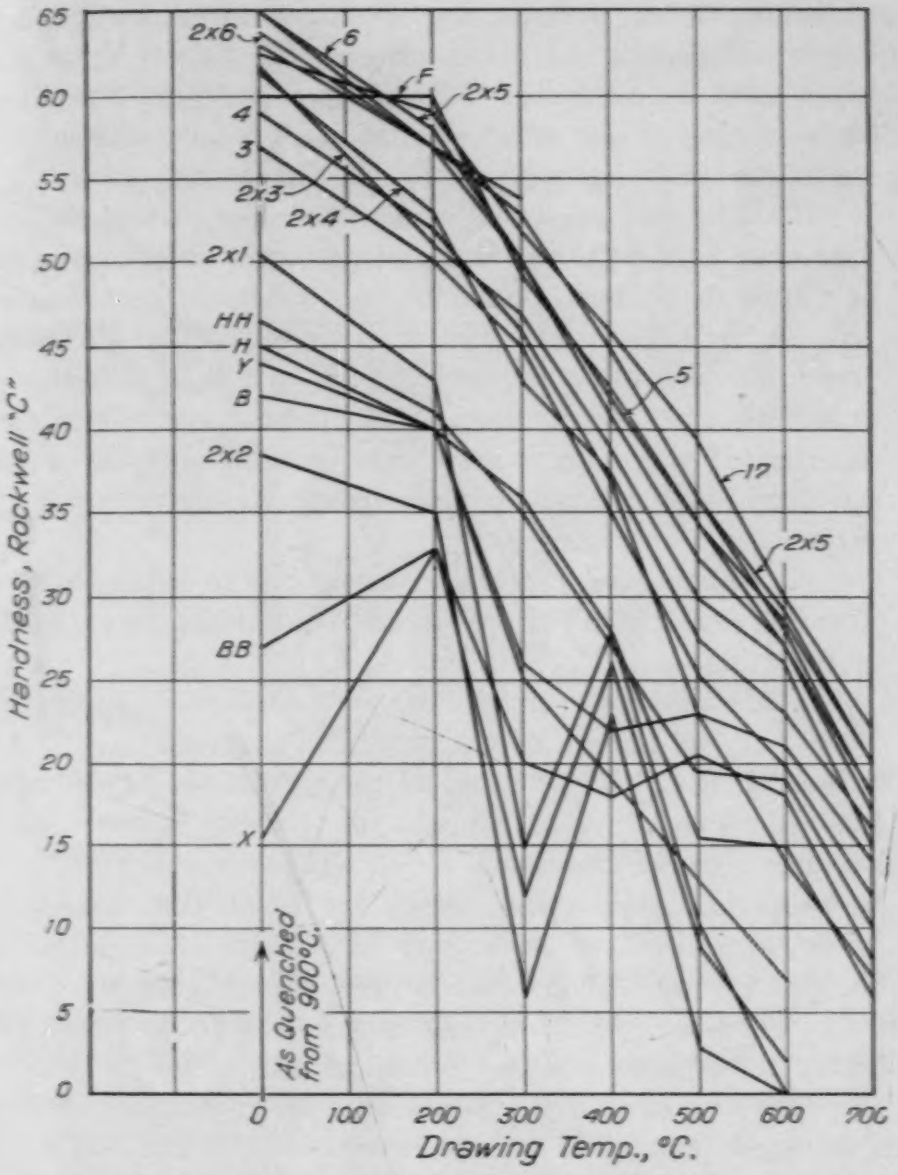

Fig. 8—Rockwell C Hardness of All Steels Tested as a Function of Drawing Temperatures.

step of knot formation which has been proposed by Merica,[6] and others to account for the so-called induction period in certain nonferrous dispersion hardening alloys. Our hypothesis of internal surface formation receives some support from the X-ray investigations of Burgers and Snoek.[7] These investigators found that while the coercive force is increasing, the type

[6]Paul D. Merica, "The Age Hardening of Metals," Annual Lecture A.I.M.E., Institute of Metals Division, 1932.

[7]W. G. Burgers, and J. L. Snoek, "Lattice Distortion and Coercive Force in Single Crystals of Nickel-Iron-Aluminum," *Physica*, Vol. 2, p. 1064-74, 1935.

of line broadening indicates the "Formation of regions of slightly larger and slightly smaller spacing in the matrix lattice which has not lost its coherence." This step is doubtless accompanied by hardening of the order of that produced by cold work but the major hardening arises from the next step.

2. *The second phase precipitates at the internal surface so formed and produces hardness by keying.* In order to precipitate as a separate phase in the continuous solid solution the internal pressure[8] of the solvent lattice must be overcome. This internal pressure is enormous for solid metals and is an effective hindrance to such precipitation. Just as steam bubbles form in superheated water much more readily at an interface so does the new phase precipitate much more readily at an internal surface.

3. *Internal surface heals, causing a drop in coercive force.* This is crystal growth of the solvent lattice usually brought about by reheating.

4. *Precipitated particles of the second phase agglomerate.* This is crystal growth of the precipitating phase.

In quenching a solid solution, all these processes of decomposition may take place. What happens on reheating depends on the relative rates of these processes.

In tempering, plain carbon steels for which data have so far been given, step 3, that is, healing of the solvent lattice, takes place with the greatest rapidity up to 400 degrees Cent.; hence, the coercive force drops steadily. At 500 degrees Cent. step 1 becomes more rapid than step 3, hence coercive force increases.

Step 4 is also more rapid than 1 or 2 up to 400 degrees Cent.; hence, hardness falls. The sudden increase in step 1 at 500 degrees Cent. does not result in a hardness increase because step 4 remains faster than step 2.

Perhaps a further explanation of the concept of internal surface might clarify this hypothesis. The term "internal surface" means any discontinuity in the lattice including, of course, the interface between ferrite and austenite. It is thought that the ferrite-austenite interface accounts for only a small proportion of the coercive force. On quenching there is formed a very great internal surface as a result of volume adjustment. This internal surface is the natural point for

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[8]W. C. McC. Lewis, "Internal Molecular or Intrinsic Pressure," *Transactions*, Faraday Society, 1911, Vol. 7, p. 94-115.

the second phase (carbide) to precipitate. The internal surface so stabilized contributes to coercive force but is, according to present theory, only a small percentage of the whole. It is the remainder that is healed in the range below 400 degrees Cent. and hence accounts for the great drop in coercive force in the temperature range in which most of the austenite breaks up. This does not disagree with the well established fact that most of the austenite breaks

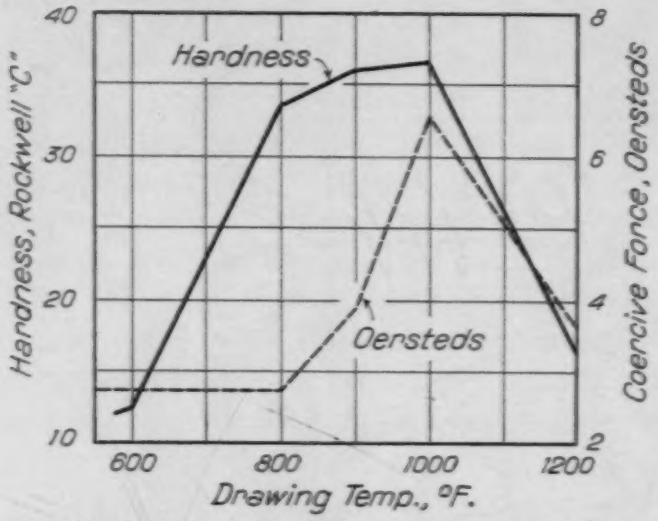

Fig. 9—Rockwell C Hardness and Coercive Force of Special Steel as a Function of Drawing Temperature.

up around 200 degrees Cent. What is postulated is that some portions of the austenite escaped forming internal surface on quenching. This austenite cannot separate carbide until a much higher temperature is reached than is the case for solid solution in which internal surface has been formed. It is this retained "continuous" austenite that decomposes at 500 degrees Cent. with the formation of internal surface and subsequent very rapid precipitation and growth of carbide in some of this surface.

Coercive Force and Rockwell Hardness of Special Age-Hardening Steel after Various Heat Treatments

To check the usefulness of these postulates regarding the mechanism of dispersion hardening a steel was used which had hardening properties very different from plain carbon steel. Through the kindness of F. B. Foley, superintendent of research of the Midvale Steel Co., a steel of the compostion which is herewith shown

	Per Cent
Carbon	0.04
Manganese	0.20
Silicon	0.24
Nickel	5.13
Aluminum	2.39

was made available. The results obtained are illustrated in Fig. 9.

It will be seen that the material as quenched has a relatively high coercive force and low hardness. On tempering at 600 to 800 degrees Fahr. the hardness increases sharply while the coercive force remains constant. Above 800 degrees Fahr. the coercive force increases rapidly reaching a maximum rate of increase with drawing temperature after the rate of increase of hardness has fallen off. The explanation in the light of the hypothesis proposed is that by quenching, the alloy has formed a relatively large internal surface indicated by high coercive force and that the remaining undecomposed solid solution is stable up to 800 degrees Fahr. Accordingly, in the range 600 to 800 degrees Fahr. only step 2 takes place, that is, precipitation of the second phase at the internal surface with increased hardness. Above 800 degrees Fahr. the solid solution breaks

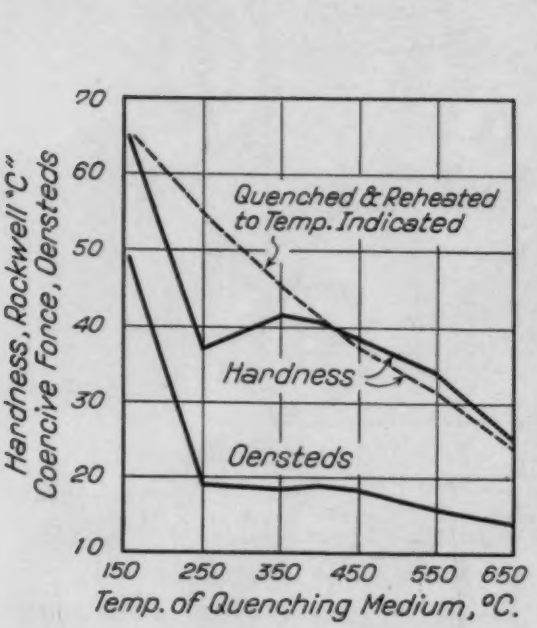

Fig. 10—Hardness and Coercive Force of 0.9 Per Cent Carbon Steel Quenched from 850 Degrees Cent. into a Bath at Various Temperatures, also the Hardness After Quenching in Water and Drawing to Various Temperatures.

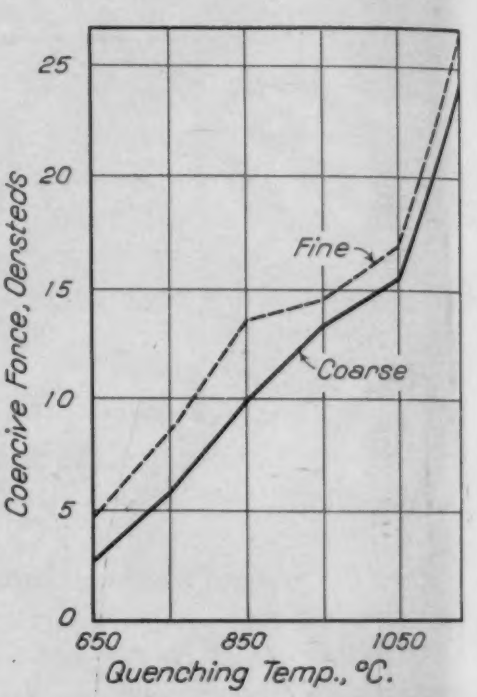

Fig. 11—Effect of Quenching Temperature Upon the Hardness and Coercive Force of "Fine" and "Coarse"-Grained Steel of 0.18 Per Cent Carbon Content.

up with a sharp increase in coercive force but step 4 has increased in rate to such an extent that there is very little hardening.

Effect of Quenching into a Bath at Elevated Temperatures

An eutectoid steel was quenched from 850 degrees Cent. into a bath at various temperatures from 200 to 650 degrees Cent., and the hardness and coercive force were measured. The results are shown in Fig. 10.

It would be expected that this procedure would greatly decrease the rate of step 1 at a given temperature compared to the procedure of quenching to room temperature and reheating, since the driving force due to supersaturation is decreased. This is borne out by the results on coercive force, which show that step 3 is more rapid than step 1 at all temperatures studied, and the coercive force never rises appreciably above that for annealed material. The hardness, on the other hand, is determined by the relative rates of steps 2 and 4, which are not greatly affected by the different paths by which a given temperature is reached. Only at the lowest temperature is there a considerable lowering of hardness due to quenching to an elevated temperature. This is probably accounted for by the failure of step 1 to keep pace with step 2 so that the hardening process is retarded by the unavailability of internal surface. This increase of stability of solid solution with decreased severity of quenching has often been recognized in other dispersion hardening alloys. Dean, Zickrick and Nix[9] showed that with lead-antimony alloys, slow cooling produced a metastable solid solution which decomposed; as indicated by hardening and resistance change much more slowly than a solid solution of the same composition produced by quenching.

Effect of Fine and Coarse Grain on Quenched and Tempered Low-Carbon Steels

Fig. 11 shows the coercive force of fine- and coarse-grain steels after quenching at various temperatures up to 1150 degrees Cent. The fine grain shows a consistently higher coercive force. This increased coercive force of the fine-grained steel is even more sharply brought out by quenching at still higher temperatures. These results, together with those for hardness and coercive force after drawing

[9]R. S. Dean, L. Zickrick, and F. C. Nix, "The Lead-Antimony System and Hardening of Lead Alloys, *Transactions*, American Institute of Mining and Metallurgical Engineers, 1926.

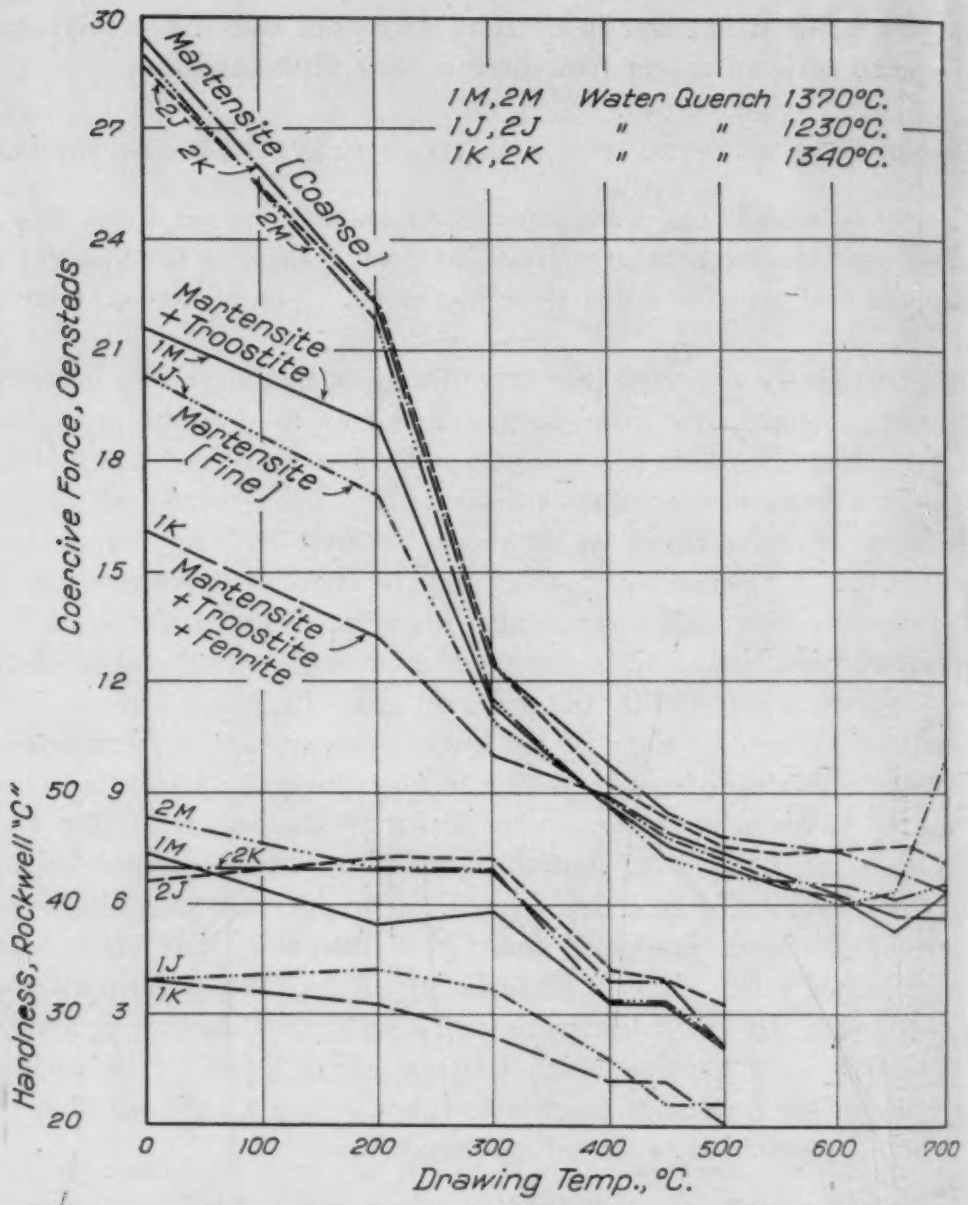

Fig. 12—Effect of Tempering Upon the Coercive Force of Plain Carbon Steel of 0.18 Per Cent Carbon Content Previously Quenched from Various Temperatures.

at various temperatures, are given in Fig. 12. The fine-grained steel gives almost the same coercive force quenched at 1230 degrees Cent., 1370 degrees Cent., or 1340 degrees Cent., while the coarse-grained steel gives values from 16 to 22 oersteds with the minimum for the 1340 degrees Cent. quench.

This lower coercive force of the coarse-grained steel is, according to our hypothesis, due to the fact that in coarse-grained steels steps 1 and 2 are slowed down relative to steps 3 and 4. As a result,

both agglomeration and healing take place more rapidly than internal surface formation and keying so both hardness and coercive force are materially reduced as compared to fine-grained steel. In general, the reduction in coercive force for the coarse-grain is greater than the reduction in hardness.

It is probable that step 1 is not actually slowed down in coarse-

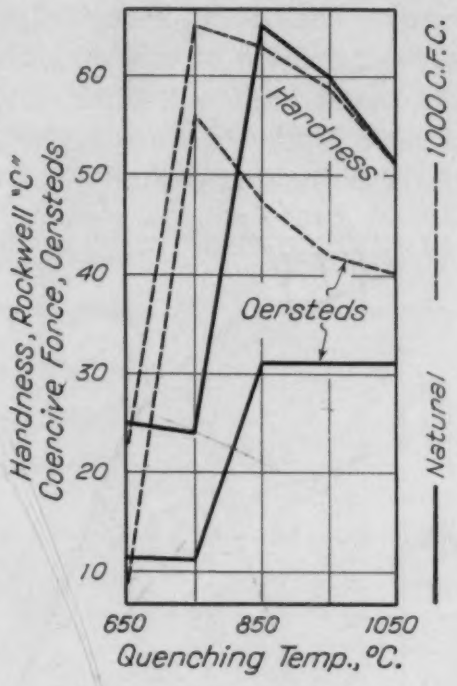

Fig. 13—Effect of Previous Treatment Upon the Relation Between Coercive Force, Hardness and Quenching Temperature of a 0.95 Per Cent Carbon Steel.

grained steel but is merely rendered in a measure unnecessary in fine-grained steel by the inchoate existence of considerable internal surface. In both fine and coarse steel quenched from high temperatures the coercive force falls off rapidly up to a drawing temperature of 300 degrees Cent. where the fine and coarse quenched steels have approximately the same coercive force. This indicates that there is no difference in the nature of internal surface in fine- and coarse-grained steels but merely that step 3 has proceeded further in the case of the coarse than the fine grain. As already indicated, step 4, or agglomeration of carbide, takes place more slowly than healing so that hardness falls very little on drawing to 300 degrees Cent.

The Effect of Structure Prior to Final Treatment on the Coercive Force and Hardness of an Eutectoid Steel

Fig. 13 shows the coercive force and hardness after quenching from various temperatures of a 0.95 per cent carbon steel in the annealed, as-rolled and furnace cooled condition. The hardness on quenching from 850 degrees Cent. or above is not greatly different for the two kinds of specimens. The coercive force is much greater, however, for the furnace cooled and hence originally coarse-grained specimens. The only explanation of this somewhat surprising result is that a large homogeneous grain will super cool further and hence break down into a finer block structure on appropriate quenching than the smaller less homogeneous grain.

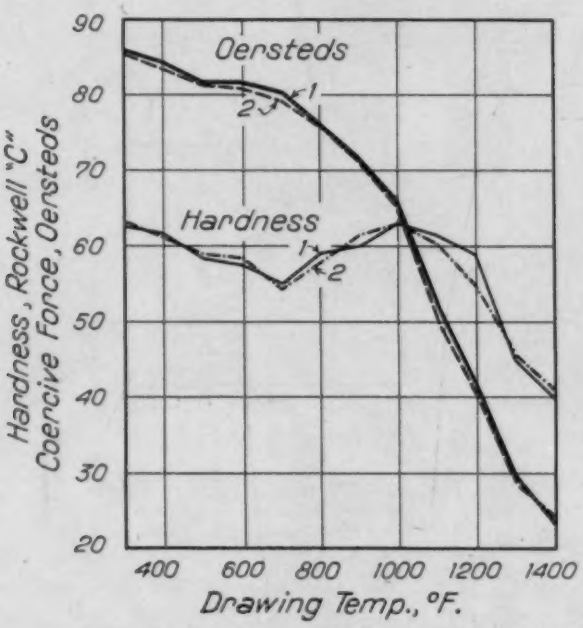

Fig. 14—Changes in High Speed Steel Upon Tempering—Coercive Force and Hardness.

Coercive Force and Hardness of High Speed Steels

The case of high speed steel is an interesting example of the disparity between mechanical and magnetic hardness spoken of in the introductory paragraphs of this article.

As would be expected, the carbides resist agglomeration up to 1200 degrees Fahr., and hence the hardness is not lowered, while the coercive force falls approximately one-third of the value in the quenched material by drawing to this temperature.

These results are shown in Fig. 14. The drop in coercive force

is attributed to heating of the internal surface of the ferrite matrix without agglomeration of the carbide particles.

Coercive Force of Rolled Steels as a Function of Carbon Content

The ease and rapidity of coercive force determinations with the coercimeter suggest that the instrument might be used as a shop-control method for carbon content. With this thought in view, a series of open hearth rimmed steels of C content ranging from 0.05 to 0.14 were obtained from the Laclede Steel Company. The results of the tests in the as-rolled condition are shown in Fig. 15.

The possibilities of developing shop control of heat treatments by coercive force measurements are very promising and are being studied further. For example, in the patenting of wire it is well

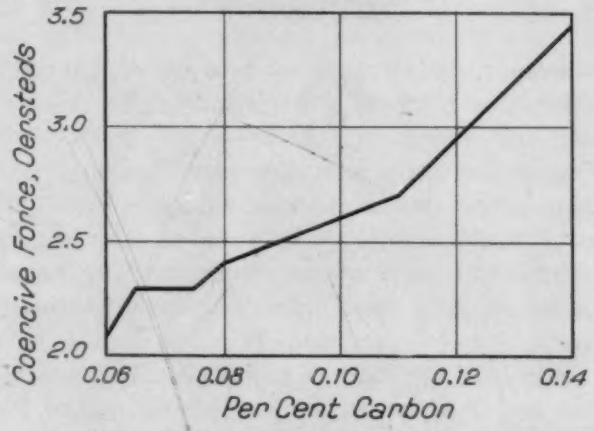

Fig. 15—Relation Between Coercive Force and Carbon in Some Samples of Rimmed Steel (Laclede).

known that wire of the same composition and hardness reacts very differently to further drawing, depending on whether the hardness is obtained by quenching and drawing or by quenching in a bath at elevated temperatures. The wire which has been quenched in a bath at high temperature is much more ductile as would be indicated by its lower coercive force and hence internal surface. In cases of this kind, coercive force should prove a useful method of inspection and shop control.

Summary

The lack of parallelism between magnetic and mechanical hardness in steels has been confirmed. To explain the relation between

hardness and coercive force in steels subjected to various treatments the hypothesis is offered that in the hardening and drawing of steel the following steps take place:

1. The grains break down into blocks, thus forming internal surface which greatly increases coercive force.
2. The second phase is precipitated at the internal surface and greatly increases hardness.
3. The internal surface heals causing reduced coercive force.
4. The precipitated phase agglomerates causing decreased hardness.

Possible uses of coercive force as a shop-control method are suggested.

DISCUSSION

Written Discussion: By W. L. Fink and D. W. Smith, Research Laboratories, Aluminum Company of America, New Kensington, Pa.

This interesting and illuminating paper on the mechanism of steel hardening and tempering by Dr. Dean and Professor Clayton expresses, in slightly different terms, conclusions similar to those which we have made concerning the age-hardening of aluminum alloys in a series of papers presented before the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. The most recent of these is to be presented during this convention.

It has been shown that, during rapid quenching of aluminum-copper alloys containing 4 and 5 per cent copper, plastic deformation takes place. The deformation is sufficient to cause the appearance of slip-bands on the surface of a previously polished sample. The discussers suggest that the formation of "internal surfaces" during the quenching of steel (the first structural change as postulated on the sixth page) is accounted for by plastic deformation rather than by the formation of "knots."

In the investigation on the age-hardening of rapidly quenched aluminum-copper alloys, the earliest microscopic evidences of precipitation of a second phase are shown to appear along the previously formed slip-bands before any substantial hardening occurs. Continued aging of these alloys results in a primary hardening peak. This is in accordance with the second structural change postulated by Dean and Clayton. Aging for slightly longer times results in some softening. This may be caused by either step three or four (within the plastically deformed regions). Still further aging produces a second hardening peak which is accompanied by general precipitation of the Widmanstätten type in those regions of the grains which have not suffered plastic deformation during the quench. This latter hardening is not adequately explained by the four proposed steps in the hardening processes.

It is to be hoped that the authors will continue these interesting investigations and that changes in hardness and coercive force will be determined as functions of time at constant drawing temperatures. With these last mentioned results probably even greater similarities will be evident between the hardening processes in steel and the strong aluminum alloys.

Oral Discussion

PROF. L. W. MCKEEHAN:[1] Is there any way in which we can see why coercive force and surface could be related. I think there is a possible connection. Coercive force by itself is rather an anomalous thing. The theories generally wander around without telling us there should be any coercive force in a homogeneous crystal, and in the case of part of a grain which is near the boundary, or part of a free crystal which is near the boundary, or part of a polycrystalline sample which is near the boundary, there are certainly differences in the state of what we may call internal stress and strain, as compared with the central parts of these structures where everything is much more symmetrical, where the atoms are surrounded similarly and by great numbers of neighbors.

We only have to remember that at the surface the atoms are under one-sided control; that the problem of changing the direction of magnetization and therefore the net magnetization, as measured outside, is different near the surface.

We know that a great many materials, including most of those capable of study here, are strain-sensitive in their magnetic behavior; that is, arbitrary stresses change, among other things, the coercive force.

I am just suggesting that at the surfaces of these homogeneous regions, which are small, the problem of changing the direction of the magnets so as to either create or destroy a net magnetization is a harder problem than if the material is homogeneous, continuous and alike in all its parts. That is, a state of superficial strain in each small region is an explanation for the parallelism between coercive force and total particle area.

PROF. W. R. HAM:[2] Dr. McKeehan's remarks gave me courage to say a few words. There is one point that does not seem to be brought out by the metallurgists that should be important, and that is the recognition of the fact that the iron atoms may undergo transformations. I am not a metallurgist but I am interested in the behavior of relatively pure iron. None of you would have any doubt that the iron atom undergoes a change in the Curie region. There is some doubt, it is true, as to whether the iron atom undergoes a change when we have the body-centered form change to face-centered.

However, there is a very strong evidence at present that the iron atom does undergo at least two changes in the ordinary temperature range, one near the point which you have called a "sub-zero" point. That this transformation shows up in iron nearly free from carbon I indicated from hydrogen diffusion last year. Since then several men have been investigating this very carefully with the purest iron available, and the transformation men-

[1]Yale University, New Haven, Conn.
[2]Head of Physics Department, Pennsylvania State College, State College, Pa.

tioned is always marked on any hydrogen diffusion isobar and is found between 200-350 degrees Cent., depending upon the amount of residual impurities present.

R. H. HARRINGTON:[3] Fig. 5, may I say, disturbs a sense of statistics. It shows a straight line averaging five points as far as the data are given in the curve. As a matter of fact, a very beautiful smooth curve can be drawn through these five points, and Prof. McKeehan has likewise given me courage with his recorded point. I may say he has given a possible explanation for the deviation from a straight line. I do not think it upsets at all the assumption used by Mr. Dean.

Authors' Reply

As indicated in our method of measurement, of course, we measured through the intensity of magnetization. With very definite purpose we left out of this paper any discussion of the nature of coercive force. The last thing we wish to do at the moment is to start an argument with this group which, if we may take those who have offered discussion as a fair sample, is composed of at least two-thirds physicists. Or is it that the physicists are more ready to talk than the metallurgists?

We do not agree with the idea that coercive force can be explained by strain in any sense. However, you can attenuate the idea of strain by various means until it can not be recognized, and on that basis we cannot disagree, but we are not going to discuss what exact physical conditions bring about coercive force, but will simply state that this particular gadget measures something which we think is an approximation of magnetization coercive force, and that whatever is measured seems to be proportional to the internal surface in cases where we are satisfied we can measure the internal surface.

It is possible to obtain quite high coercive forces, 400 or more, simply by powdering magnetite finely enough, and it is pretty difficult for us to imagine that strain can accomplish that much in view of the relatively small effect of cold work on the coercive force of iron.

We are very glad to have the suggestions of Professor McKeehan and Professor Ham, and are sure that you are very glad they did not allow you to go away thinking that a "B-H" curve reached saturation, or something of that kind.

[3]Research metallurgist, General Electric Co., Schenectady, N. Y.

AN X-RAY STUDY OF THE Ar_3 AND Ac_3 POINTS OF IRON AND IRON-NICKEL ALLOYS

By Sidney D. Smith

Abstract

Samples of iron and iron-nickel alloys of a high degree of purity and homogeneity were prepared by precipitation of the hydroxides which were subsequently reduced in pure hydrogen and worked to form wires or ribbons as desired. These wires or ribbon samples were heated under carefully controlled conditions of temperature in an atmosphere of pure hydrogen and X-ray photographs made of the diffraction patterns using Coolidge X-ray tubes with molybdenum targets. Practically monochromatic radiation was obtained by using zirconium oxide filters.

The value of a reversible A_3 point for iron of high purity and values for the Ar_3 and Ac_3 points of iron-nickel alloys containing up to 5.3 per cent nickel were determined.

IT is well known that investigations of the A_3 points of iron and iron alloys have been hampered by the lack of homogeneity of the specimens used (1), (2), (3), (4)[1]. The purpose of the present work is to extend the observations of Roberts and Davey (4) using the same precautions that they did to insure extreme purity of the specimens and to give every possible opportunity for homogeneity from point to point. Roberts and Davey reported a reversible A_3 point for pure iron and gave data for irreversible A_3 points for iron-nickel alloys with ascending temperatures (Ac_3 points). This paper not only confirms their work but also extends it by reporting the A_3 points for descending temperatures (Ar_3 points).

Preparation of Specimens

Two fine jets of (a) an aqueous solution of ammonium hydroxide and (b) an aqueous solution of ferric nitrate and nickel nitrate

[1]The figures appearing in parentheses pertain to the references appended to this paper.

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. From a thesis submitted to the Department of Chemistry of the Graduate School of The Pennsylvania State College in partial fulfillment of the requirements for the Ph.D. degree. The author, Sidney D. Smith, is now with E. I. duPont de Nemours and Company, Belle, (Charleston), West Virginia. Manuscript received June 21, 1937.

were caused to swirl together in air. This resulted in an exceedingly intimate mixture of ferric and nickel hydroxides which was washed with freshly distilled water until a negative test for electrolytes was obtained. The hydroxides were then dried to the oxides and reduced by heating at about 600 degrees Cent. (1110 degrees Fahr.) in an atmosphere of dry, oxygen-free hydrogen. This method of preparation gave every opportunity for a uniform mixture of fine particle size and subsequent steps gave further opportunities for the diffusion of the nickel. The reduced metal powder was compressed, sintered and swaged, using the same technique as in the commercial manufacture of tungsten rods. The specimen was then drawn to wire or rolled to ribbon as desired. The result was a series of wires and ribbons of definite nickel content and of extremely high purity.

This process offers extraordinary precautions against lack of homogeneity. The fact that the original hydroxides were precipitated in a fine swirl tends toward at least an exceedingly intimate mixture of fine-grained particles of ferric and nickel hydroxides, or possibly, even a double hydroxide. Subsequent drying to the oxides tends to give, if not a solid solution of nickel and ferric oxides, at least a still finer grained mixture than that obtained for the hydroxides. The reduction of this intimate mixture of oxides without melting, should involve enough atomic motion to render the metal still more homogeneous than the oxides. The swaging and drawing (or rolling) should still further homogenize the metal.

It is believed that, in point of homogeneity, the specimens used in this work represent the limit attainable at present for the iron-nickel system. A brief metallographic examination of specimens gave results consistent with this picture.

A preliminary spectroscopic analysis of a typical iron specimen was made through the kindness of Mr. M. L. Fuller of the New Jersey Zinc Company. This revealed lines for the following elements:

Al—very faint
Mg—very faint
Si—faint
Mn—weak
Cu—very faint (a trace of copper was present in the control test of the graphite electrode).

Additional elements which were looked for but not found were: Li, Ag, Au, Be, Ca, Ba, Zn, Cd, Hg, B, Ga, In, Tl, Ti, Ge, Sn, Pb, P, V, As, Sb, Bi, Cr, Mo, Se, Te, Co, Pt. It is believed, although

not definitely proved, that this specimen was at least 99.94 per cent iron[2].

Chemical analysis for nickel was made by the dimethyl glyoxime method. For every composition four independent analyses were made. In every case the four checked within 0.2 per cent.

Apparatus

At temperatures above 700 degrees Cent. (1290 degrees Fahr.) the apparatus used was similar to that used by Roberts and Davey (4). The specimen and film were mounted under a water-cooled

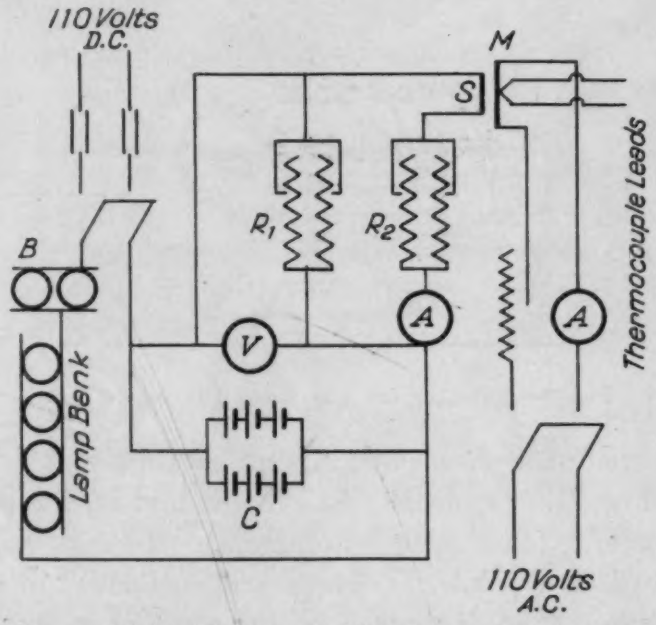

Fig. 1—Wiring Diagram of High Temperature Apparatus.

bell which was filled with dry, purified hydrogen to prevent oxidation of the specimen when heated. Measurement of the temperature was made by means of a calibrated fine gage platinum, platinum-rhodium thermocouple attached to an electrically heated ribbon (M, Fig. 1) whose composition was identical with that of the specimen (S, Fig. 1). A color match between the specimen and the ribbon enabled the temperature of the specimen to be read to within $\pm$ 2 degrees Cent.

The electrical circuit for heating the specimen is shown in Fig. 1. The current was set and maintained closely to a constant value with the aid of General Electric B46, ballast tubes (B, Fig. 1). The storage battery, C, which was floated across the ballasted line made

[2]Spectrographic analysis of a similar batch gave the following estimated impurities in per cent, Co, 0.01; Cu, 0.005; Mn, 0.01; Si, 0.005; C, 0.005; Mg, 0.0001; Ca, 0.001; Sn, 0.001; Mo, trace; Cr, trace; Al, trace. Total impurities, probably of the order of 0.04

the heating current still more constant. Current in excess of that desired through the specimen was shunted out through the resistance, R_1. Thus the temperature of the specimen could be set and maintained constant within the error of measurement, estimated at ± 2 degrees Cent., for an indefinite period.

Since an accurate comparison of the color of the heated specimen and ribbon was not possible at temperatures much below 700 degrees Cent. (1290 degrees Fahr.), a different form of apparatus was used at lower temperatures. This apparatus is shown in Figs. 2 and 3.

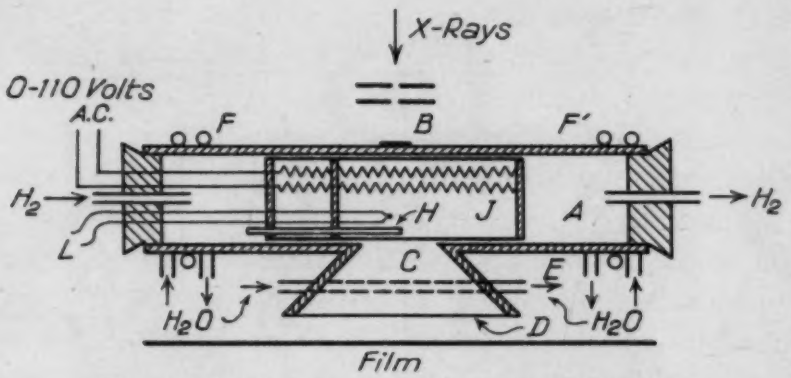

Fig. 2—Apparatus for Use Below 700 degrees Cent.

It consisted of an iron pipe, A, on the front of which was placed a mica window, B. Opposite this window and on the back side was fastened a hollow, fan-shaped iron piece, C. To the outer end of this was fixed a paper window, D, which was shellacked to render it gas tight. A cooling tube, E, brazed on the top and bottom of this fan-shaped piece kept the window cool. The central portion of the tube, A, was lagged to prevent heat loss while the ends were kept cool by the cooling coils, F-F'. The ends of the tube were closed by rubber stoppers through which passed the hydrogen delivery and exit tubes, electrical leads to heating element and chromel-alumel thermocouple leads, L.

The specimen, G, was suspended in a heavy brass holder, H. This was supported on an insulated frame, I, which also carried the heating element and chromel-alumel thermocouple. The frame fitted into the pipe, A, very snugly. The heating element had a maximum rating of 1000 watts and was connected in series with appropriate resistances so that the current could be adjusted as desired. Current was drawn from a generator whose capacity was high in comparison to the load it carried and since the heat capacity of the apparatus was

quite large, temperature variations were small. Attainment of temperature equilibrium for the apparatus was slow and could not be held closer than ± 3 degrees Cent.

The delay in attaining temperature equilibrium was partly compensated for by using the recently developed "Fluorzure" intensify-

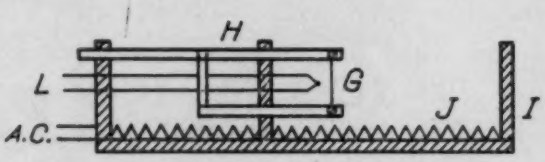

Fig. 3—Side View of Specimen Holder.

ing screens in conjunction with the photographic films. Due to the use of these screens the length of exposure time was shortened from about 72 to 24 hours.

Coolidge X-ray tubes with molybdenum targets were used. These were operated on 30 kilovolts and a tube current of 25 milliamperes. A zirconium oxide filter placed in front of the slit system rendered the x-radiation practically monochromatic.

Procedure

The procedure followed at temperatures above and below 700 degrees Cent. (1290 degrees Fahr.) was very similar. In determining the Ac points the specimen was heated until it was slightly below some predetermined temperature and then slowly raised to that temperature. For the Ar points the temperature was raised above some predetermined temperature and then slowly lowered to the temperature at which the diffraction pattern was to be taken.

At higher temperatures the photographic film was placed in position, the bell placed over the apparatus and the interior filled and flushed with hydrogen. Current was then permitted to flow through the specimen circuit until the ballast tubes and specimen holder were thoroughly warmed up at a temperature near that desired. The specimen was then set at the desired temperature and this was checked for constancy. In heating to a desired temperature the time of each step in the procedure was kept approximately the same. Once the apparatus was finally adjusted the temperature remained constant within the experimental error (± 2 degrees Cent.) throughout the exposure of the film.

The procedure with the lower temperature apparatus was substantially the same. In this case, the photographic film was outside

the apparatus and the furnace was always filled with hydrogen. The heat capacity of the furnace was rather large so that considerable time was required to reach any desired temperature. From frequent checks the variation of temperature during an exposure was estimated as ± 3 degrees Cent.

Diffraction patterns were taken on Eastman "Ultra-speed duplitized contrast" X-ray films held in a flat watercooled holder. For temperatures below 700 degrees Cent. "Fluorazure" intensifying screens were used. The specimen-to-film distance was determined by calculation from the diffraction patterns of both sodium chloride and pure (supposedly at least 99.94 per cent) iron.

The type of pattern (i.e., body-centered or face-centered cubic) was determined by visual inspection and confirmed by quantitative measurement of the lines on the film.

Results

For each of the alloys tested, a large number of diffraction patterns was taken. Tables I to IV show data from such of the patterns as turned out to be taken immediately above and below the Ac_3 and Ar_3 points. The cumulative evidence of the other patterns, (not included in Tables I–IV), is, of course, of great weight in showing that really sharp transition points were found.

A reversible A_3 point for pure iron was found between 907 and 908 ± 2 degrees Cent. This agrees with the value reported by Roberts and Davey (4) who found it to fall between 907 and 910 degrees Cent. (1665-1670 degrees Fahr.), but is lower than that of 928 ± 2 degrees Cent., which Austin and Pierce (5) believe represents this critical point. The value of 928 degrees Cent. was later changed to 910 degrees Cent. (6). Their samples were obtained from carbonyl iron and measurements were made with a vacuum interferometer. The methods and technique of the present experiments yield specimens of high purity, having a reversible A_3 point which can be reproduced from time to time.

The A_3 points for the iron-nickel alloys were not reversible. In all cases the Ac_3 points were higher than the Ar_3 points. This is consistent with ordinary metallurgical experience. The separation is, however, not great (about 14 to 15 degrees). It is possible that this spread is caused by some remaining inhomogeneity in the specimens. This is not considered probable in view of the method of manufacture of the specimens.

Table I
A_3 Points For Pure Iron

Film	Ar Points Degree Cent.	Structure	Film	Ac Points Degree Cent.	Structure
F3-2	911	FCC	F4-1	905	BCC
F3-3	910	FCC	F4-3	906	BCC
F3-5	908	FCC	F4-4	907	BCC
F4-6	907	BCC	F4-5	908	FCC

Table II
A_3 Points For Iron-Nickel (2.0%)

Film	Ar Points Degree Cent.	Structure	Film	Ac Points Degree Cent.	Structure
F2N-14	758	FCC	F2N-9	772	BCC
F2N-13	757	BCC	F2N-8	773	FCC
F2N-12	755	BCC	F2N-7	775	FCC

Table III
A_3 Points For Iron-Nickel (3.13%)

Film	Ar Points Degree Cent.	Structure	Film	Ac Points Degree Cent.	Structure
F4N-16	705	FCC	F4N-1	Room	BCC
F4N-18	704	BCC	F4N-10	710	BCC
F4N-17	700	BCC	F4N-11	712	BCC
			F4N-12	713	BCC
			F4N-13	714	FCC

Table IV
A_3 Points For Iron-Nickel (5.30%)

Film	Ar Points Degree Cent.	Structure	Film	Ac Points Degree Cent.	Structure
F8N-3	617	FCC	F8N-10	616	BCC
F8N-5	608	FCC	F8N-11	620	BCC
F8N-8	605	BCC	F8N-14	622	FCC

The Ar_3 and Ac_3 points for pure iron and iron-nickel alloys are summarized in Table V and these results are shown graphically in Fig. 4.

Summary

1. The value of a reversible A_3 point for iron of high purity as reported by Roberts and Davey (4) is confirmed as being between 907 and 908 $\pm$ 2 degrees Cent.

2. Values for the Ar_3 and Ac_3 points of iron-nickel alloys are given.

Table V
Summary of Temperatures for Ac_3 and Ar_3 Points

Composition of sample	Ar Point	Ac Point
Fe (est. at 99.94% Fe)	908° $\pm$ 2°C	908° $\pm$ 2°C
Fe + 2.0% Ni	758° $\pm$ 2°C	773° $\pm$ 2°C
Fe + 3.13% Ni	705° $\pm$ 2°C	714° $\pm$ 2°C
Fe + 5.30% Ni	608° $\pm$ 3°C	622° $\pm$ 3°C

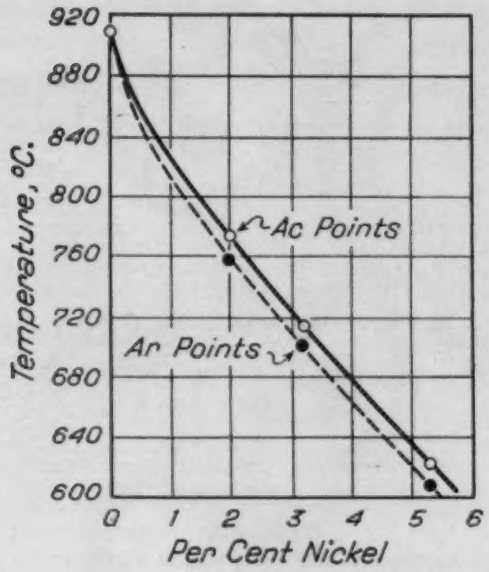

Fig. 4—Ar_3 and Ac_3 Points for Fe-Ni Alloys.

Acknowledgments

This work is a portion of investigations of the iron-nickel system for which a grant-in-aid was made by the National Research Council. Without this, the preparation of the specimens would not have been possible. It is a pleasure to express appreciation for this timely aid.

To Dr. W. P. Davey, the writer expresses his deep appreciation for the many suggestions and help which made this work possible. He also wishes to express his appreciation to Mr. Dan McLachlan for aid in making up specimens, to Mr. M. L. Fuller of the New Jersey Zinc Company for the spectroscopic analysis, and to Professor C. R. Austin for help in the micrographical portion of the work.

References

1. Burgess and Crowe, *Transactions,* American Institute of Mining and Metallurgical Engineers, Vol. 82, 665 (1913).
2. Hanson and Hanson, *Journal,* Iron and Steel Institute, Vol. 102, 1920, p. 39.
3. Westgren, *Journal,* Iron and Steel Institute, Vol. 103, 1921, p. 302.
4. Roberts and Davey, *Metals and Alloys,* Vol. 1, 1930, p. 1.
5. Austin and Pierce, Transactions, American Society for Metals, Vol. 24, 1936. p. 70.
6. Austin, Transactions, American Society for Metals, Vol. 24, 1936, p. 69.

DISCUSSION

Written Discussion: By M. L. Fuller, investigator, Research Division, New Jersey Zinc Co., Palmerton, Pa.

The spectrographic analysis given in footnote 2, page 257, of the paper

unless properly qualified may lead to an inexact interpretation of the purity of the material employed by Dr. Smith. In our original communication to Dr. Davey regarding the results of the spectrographic examination, it was stated that the analysis was only a semiquantitative estimate based on a comparison with certain available iron samples of known analysis. Oxygen or other gases and most of the nonmetals could not have been detected by the spectroscopic method employed. The estimates were further qualified as follows: cobalt, 0.01 per cent; copper, 0.005 per cent; manganese, probably less than 0.01 per cent; silicon, greater than 0.005 per cent; carbon, greater than 0.005 per cent; magnesium, less than 0.0001 per cent; calcium, 0.001 per cent; tin, less than 0.001 per cent; molybdenum, present but not estimated; chromium, 0.001 per cent or higher; aluminum, present but not estimated. In reporting this semiquantitative analysis, no estimate of total impurity content was made. This particular specimen was an iron-nickel alloy and not iron as stated in the paper.

This discussion is prompted by an evident misunderstanding by the author of the limitations of the spectrographic analysis which we performed and will serve to prevent any misinterpretation of the composition.

Written Discussion: By J. G. Thompson, National Bureau of Standards, Washington, D. C.

In citing the value 928 ± 2 degrees Cent., reported by Austin and Pierce, for A_3 in high purity iron, Dr. Smith has apparently overlooked the fact that this figure was subsequently corrected[1] to 910 degrees Cent., because of the discovery of a pyrometric error in the original observation.

A review of available information on the preparation and properties of high purity iron[2] showed that the best determinations, by a variety of methods, were in agreement that 910 degrees Cent. is the best approximation of the Ac_3 temperature in high purity iron and further showed that the spread between Ac_3 and Ar_3 becomes smaller with slower rates of heating and cooling; at very slow rates Ac_3 and Ar_3 for high purity iron practically coincide. It is gratifying to have these conclusions further confirmed by the X-ray method reported by Dr. Smith.

Written Discussion: By Cyril Wells, Metallurgical Department, Carnegie Institute of Technology, Pittsburgh.

The author's conclusions that high purity iron transforms at 908 ± 2 degrees Cent. and the transformation is reversible confirm results previously published by Wells, Ackley and Mehl.[3] Within the last few years Roberts and Davey[4] have reported the A_3 as being between 907 and 910 degrees Cent., Wells, Ackley and Mehl have shown it to be 910 ± 1 degrees Cent., Austin[5] gives it as 910 degrees Cent. and now the present author concludes it is 908 degrees Cent. With this amount of independent and apparently reliable evidence before us,

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[1]J. B. Austin. Discussion of paper by Wells, Ackley, and Mehl, TRANSACTIONS, American Society for Metals, Vol. 24, p. 69-70, 1936.

[2]The Metal Iron, McGraw-Hill Book Co., Inc., 1935.

[3]C. Wells, R. A. Ackley and R. F. Mehl: "A Dilatometric Study of the Alpha-Gamma Transformation in High-Purity Iron." TRANSACTIONS, American Society for Metals, 1935, Vol. 23, p. 46.

[4]O. L. Roberts and W. P. Davey: "X-Ray Study of the A_3 Point of Iron and Some Fe-Ni Alloys." *Metals and Alloys*, Vol. 1, 1930, p. 1.

[5]J. B. Austin: Reference 1. Discussion p. 69.

it is difficult to accept Adcock and Bristow's[6] results showing the α-γ transformation to have a range of 26 degrees Cent. on heating and 12 degrees Cent. on cooling and an average Ac_3 of about 928 degrees Cent. for the rate of heating used. The same viewpoint may be given regarding Esser's results.[7] In the case of Esser's work, one may wonder if the observed effect of hydrogen is for the most part an effect of hydrogen on his couple rather than on his iron. Of course Adcock and Bristow might show that they present more evidence of a complete analysis of materials than the present author has done, and on this basis contend that their alloys, whose total impurities were reported to be less than 0.03 per cent were purer than those used by Smith. However, since a complete analysis of a large part of the 5-pound load of No. 3 iron used by Wells, Ackley and Mehl is given, and their results are in agreement with those of the present author and not Adcock and Bristow's results, the above criticism loses much of its point, and the present discusser believes the A_3 temperature should be accepted for the present as being quite close to 910 degrees Cent.

Oral Discussion

W. P. DAVEY: I am very sorry that Mr. Fuller and I do not seem to be talking about quite the same thing. His statements apply to a specimen of iron-nickel alloy which we sent down requesting an analysis, and what I read off this morning has to do with another analysis which he made for us on our iron specimen. We have tried to take into account the figures which he has given in the case of the iron-nickel, in making our estimate of 99.96 per cent iron and nickel. We have no illusions as to the difficulty of spectrographic analysis nor the points which have to be taken into account in presenting spectrographic analysis, but we think we have taken those things into account in making our estimate of only four hundredths of one per cent total impurities.

F. M. WALTERS, JR.:[8] Dr. Smith is to be congratulated on overcoming the experimental difficulties involved in X-ray observations at elevated temperatures. The results of this investigation are of interest since they are so completely at variance with those of other observers. Studies of iron-nickel and iron-manganese alloys of purity equivalent to those prepared by Dr. Smith show that the alpha-gamma transformation occurs at a markedly lower temperature on cooling than on heating and that a two-phase region of definite width is always found. It has been observed that when a homogeneous binary alloy (iron-nickel, iron-manganese) is taken into the two-phase region and held for even so short a time as half an hour, a separation in composition occurs and the alloy is no longer homogeneous.[9] Dr. Smith's exposures took about twenty-four hours, a time ample to show the effect of diffusion. The question naturally arises, what was there about the preparation of the alloys which effectively prevented diffusion and which thus caused the alloys to be reversible?

[6]F. Adcock and C. A. Bristow: "Iron of High Purity." Proceedings of the Royal Society, 1935, A, Vol. 153, p. 172.

[7]H. Esser: "The Allotropy of Iron." Carnegie Scholarship Memoirs, Iron and Steel Institute, Vol. XXV, 1936, p. 213.

[8]Metallurgical Dept., Youngstown Sheet and Tube Co., Youngstown, Ohio.

[9]E. Scheil, *Arch. für das Eisenhüttenwesen*, V. 9, 1935-36, p. 163-166.
E. Scheil, *Arch. für das Eisenhüttenwesen*, V. 9, 1935-36, p. 115-116.
F. M. Walters, Jr., TRANSACTIONS, American Society for Steel Treating, Vol. 21, 1933, p. 1002-1013.

HOWARD SCOTT:[10] I am wondering what these patterns look like as you go through the transformation. What is the nature of the asterism? I take it these were pinhole patterns?

W. P. DAVEY: No, these were taken with the slide, so that we got patterns first and the difference between the face-centered cubic pattern and the body-centered cubic pattern is quite considerable. I am once more sorry that something seems to have slipped up somewhere in this meeting so that the preprints are not here, because it would have been so easy for everybody to have referred to the actual experimental data. Now let me illustrate the difference in the case of pure iron between the two sets of data. In the case of the face-centered cubic and the body-centered cubic stretchers, we had 280, 325 against 410, 494 and 607 as against 532. Now those are distances of the line on the film from the position of the undeviated beam on the film. Now there is not very much possibility of mistaking a distance of 4.9 cm. for a distance of 4.1 cm. There is not much chance of mistaking it for 513 cm., so the distance is well marked so there is no trouble in telling whether we had one or the other. There is one point Dr. Walters implied which should be brought out very carefully; we do not claim there was no two-phase system present; all we are justified in saying is there was no two-phase system found. Before we can tell just what that means, it would be necessary to make an extensive study of the sensitivity of the method at those temperatures that would be a long job and a difficult job. The film showed no evidence of both defraction patterns at once; according to the theory they should have been shown, and according to the diffusion experiments and the diffusion of hydrogen through iron, apparently there should be a very slight range; that is, if the diffusion of hydrogen experiments of Dr. Ham show a graph which, instead of having a break at the A_3 point, which is exactly vertical, a very steep break the middle point of which comes at the point we believed we would find the real A_3 point. Now whether that is a thing which is inherent in the diffusion of hydrogen experiments, I could not say; I am not sufficiently familiar with it, but we are safe when we say that we did not find two-phases present. We are trying to increase the sensitivity of our method.

F. M. WALTERS: I want to know why.

W. P. DAVEY: Well, I have not bothered to know much about why until I know we are right. I do not want to say that there was no two-phase present and I have not bothered to worry about why there was no two-phases present on our film, until after we have done some more experiments with higher sensitivity to see if we can really detect it. We realize that the burden of proof is on us. If we say we do not find it, the burden of proof rests with us to show that we have done everything we can to try to find the two phases. We have done everything we can so far and are still trying.

L. L. WYMAN:[11] One point has just occurred to me that I think might interest Dr. Davey, that is in making up alloys of powdered metals, particularly firing them in furnace with reducing atmospheres (hydrogen), we have found in our work at the Research Laboratory that there can be a very appreciable pickup of the silicon through silicon-hydride coming out of the furnace.

[10] Westinghouse Electric and Manufacturing Co., E. Pittsburgh, Pa.
[11] Research metallurgist, General Electric Co., Schenectady, N. Y.

W. P. DAVEY: I would like to say that we had no silica present in the firing furnace, in the reducing furnace, but we had an alundum belt on which our specimens rested and the furnace for firing was an alundum tube.

L. L. WYMAN: We have found that same thing in the furnace, and about the only way to get around it is to have some sort of container in which to put your samples inside of the furnace to protect them, and we seem to be able to get away with it that way. There is actually enough silica binder in the alundum materials to permit this silicon hydride formation, and subsequent silicon pickup unless the sample is protected. There seems to be a lack of ability to get very much data when you get into these two-phase fields. Take the work of Bradley and some of his co-workers, and also the work of Owen—there is some beautiful work done all the way across the iron-nickel system. You get results up to five per cent and then lose the alpha, and it is the same way coming at the two-phase field from the other side of the system. You begin to get down into this region in which we are interested, and you cannot follow the lines very well.

I would like to ask if there is any information available, from the nature of the diffraction rings that were present. Did you notice anything in reference to the definitions or resolution of the doublets?

W. P. DAVEY: We had difficulty in resolving the doublets, but blamed that on fine particle size.

L. L. WYMAN: I think I would be inclined to agree with Dr. Walters in his attitude on this question, particularly in view of the fact that so much work has been done on these alloys in England. We are in rather an elementary stage in our knowledge of this binary system. It is going to take a lot of work to solve this problem. With some English investigators, the best they could obtain at high temperatures, was a slight discoloration of the surface and diffuseness of lines. They had to go at it again, but if they did not have this discoloration they got proper resolution from filings, so we have much to learn not only in technique but also from fundamental facts concerning this iron-nickel system.

SOLUBILITY OF COPPER IN THE GRAIN-BOUNDARY MATERIAL OF A SOLID SOLUTION OF COPPER IN ZINC

By George R. Dean and Wheeler P. Davey

Abstract

A technique has been developed for obtaining, in a form suitable for spectrographic chemical analysis, specimens of material representing primarily crystal-boundary material which may be compared with other specimens of material from the body of the crystals themselves. Specialized equipment, developed for this purpose, has been shown by means of diagrams.

By spectrographic chemical analysis it has been shown that the concentration of solute in a solid solution is different at the intercrystalline boundaries than it is in the body of the crystals.

It has been shown specifically that Cu is more soluble in the body of the crystals of solid solutions of Cu in Zn than in the intercrystalline boundaries of those same solid solutions.

Introduction

PHYSICAL metallurgists have assumed, but apparently have never directly proved[1] that the composition of the interior of crystals of a solid solution differs from that of the grain boundary. The importance of this picture, if true, is obvious. It is the purpose of the present work to show direct experimental evidence of such a difference in composition, and to describe the technique used in obtaining the data.

The actual amount of material available for analysis is extremely small necessitating a micro-analytical technique. The success of quantitative spectrographic analysis in the region of small concen-

[1]Various workers (1), (2), (3), (4) have suggested the idea. Their conclusions have, in every case, been based on indirect evidence. Probably the most nearly direct evidence is given by work of the type of Phillips and Brick (2), and of Wiest (1).

From a thesis submitted to the Chemistry Department of the Graduate School of The Pennsylvania State College in partial fulfillment of the requirements for the Ph.D. degree.

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. Of the authors, George R. Dean is associated with the Miner Laboratories, Chicago, and Wheeler P. Davey is Research Professor of Physics and Chemistry, Pennsylvania State College, in charge of training of Industrial Physicists. Manuscript received June 21, 1937.

trations prompted the use of this technique in this investigation. Samples of the order of 0.5 milligram of a solid solution containing 1 to 2 per cent of alloying constituent can be analyzed quickly with the spectrograph. The use of the homologous line pair method (7), (8), (9)[2] provides an accuracy of about 10 per cent. This was found sufficient for this investigation.

Materials and Technique

Solid solutions in the high zinc portion of the copper-zinc system were used. The eta phase of the copper-zinc system consists of solid solutions of copper in zinc up to a solubility limit of 2.7 per cent. The zinc used was a special batch of high purity supplied by the New Jersey Zinc Co. This was redistilled under high vacuum by slow evaporation in a pyrex tube heated in an electric furnace. The copper used was Baker's "special reagent" grade.

A considerable quantity of a more concentrated alloy (4 per cent) was first prepared. This was made up by melting required amounts of zinc and copper in a pyrex tube under a flux of zinc chloride, the melt being vigorously stirred with a carbon rod. Tests showed complete absence of $ZnCl_2$ and of Cl^- in the ingot. The resulting alloy was analyzed quantitatively by ordinary wet analysis methods to check the copper content. For the final solid solution a portion of the concentrated alloy was melted and diluted with the required amount of zinc. In every case, analysis of a one gram sample cut from the top, and of a second one gram sample cut from the bottom of the ingot differed by not more than 1 per cent of the total copper content.

The resulting solid solutions were in all cases remelted in a pyrex tube and subjected to slow cooling in an electric furnace. The alloy was allowed to cool through the melting range at a rate of about 1 degree per hour until a temperature of 410 degrees Cent. (770 degrees Fahr.), (approximately 10 degrees below the solidus), was reached. The temperature was then held constant for 24 to 48 hours. Finally the specimen was quenched in cold water. A comparison of Hansen and Stenzel's work (5) at 400 degrees Cent. (750 degrees Fahr.) with the accepted constitution diagram for copper-zinc (6) shows that the time of anneal was amply sufficient for our purpose.

[2]The figures appearing in parentheses refer to the bibliography appended to this paper.

Typical specimens have been made up under various protective atmospheres. During the first part of the investigation ampoules of the alloy were sealed off in vacuo after a previous degassing treatment below the melting point. Measurements were made as well on samples prepared in atmospheres of hydrogen and nitrogen. Alloys with concentrations approaching the solubility limit required more drastic quenching than those of lower concentration. For this purpose the pyrex tube, open at the top, was fitted loosely into an iron pipe, and the quenching water was run directly into the pipe. Where closed pyrex tubes were employed the ampoules were dropped directly into a vessel of water. For a given composition of specimen, all these specimens gave identical final results.

After the above heat treatment the alloy was carefully sawed in two and the faces ground and polished. The surface was etched with a one-to-one mixture of concentrated ammonium hydroxide and hydrogen peroxide (3 per cent). Etching with vigorous agitation by this reagent brought out the grain structure without grooving the grain boundaries enough for a groove to be detected at a magnification of 500 diameters. The average size of crystal grains was of the order of 5 millimeters. The area of the whole etched surface was of the order of 3 square centimeters.

Means for removing a representative portion of the grain boundary material necessitated the development of a micro-technique. Among the preliminary attempts may be mentioned:

(1) Cutting material out of grain boundaries with an engraving tool. The cut was too wide, so that too much crystalline material was included in the final specimen.

(2) Coating the crystal with paraffin, cutting away the paraffin over the grain boundaries and etching with nitric acid. There was a preferential solution of zinc due to local electrolytic action.

(3) Coating the crystal with paraffin, cutting away the paraffin over the grain boundaries, and etching with various types of electrolytes such as NH_4OH, H_2SO_4, KCN. Various buffer solutions were also tried.

The procedure finally adopted was as follows: The surface of the specimen was coated with bakelite lacquer which gave a thin insulating film. Under a microscope at 25 diameters the lacquer was cut through over the grain boundary by means of a sharp steel stylus, thus exposing the metal at the grain boundary. Every effort was made to make the cut only in the bakelite film. Too great pressure

on the stylus was, however, not serious for, instead of chiseling out metal, it merely plowed a tiny furrow in the surface. Using the alloy thus prepared as the anode and a 1 x 1 centimeter square of platinum foil as the cathode, the sample was electrolyzed for a time sufficient to electrolyze into solution a definite quantity of alloy. The electrolyte used was a buffer of sodium acetate[3] and acetic acid of pH 5.0. At this pH the rate of solution of metal into the electrolyte was negligibly slow except when the current was on.

The electrolyte etching was carried out in a specially designed glass cell, (Fig. 1), in order that potentials of from 10 to 25 volts

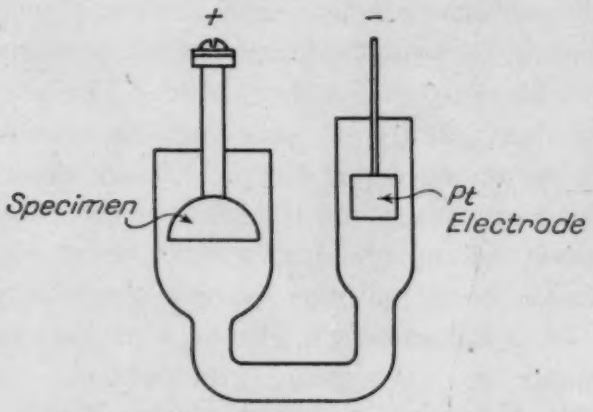

Fig. 1—Temperature vs. Loss in Weight.

could be used without passing a larger current than 2 to 3 milliamperes. This made possible a rather precise control of the weight of material removed. The solution and the platinum cathode were then transferred to a micro-electrolytic cell, (Fig. 2), provided with rapid circulation by means of an air-lift, and such copper and zinc as remained in the solution were plated out on the platinum foil. In order to be certain that substantially all the copper and zinc were plated out from the solution, the foil was weighed on a micro-balance and the actual weight of the deposited material was compared with that calculated from the number of Faradays passed through the first cell. Obviously, since the material was composed of 98 per cent or more of zinc, only a negligible error was introduced by assuming 100 per cent zinc in these calculations.

The copper-zinc deposit on the platinum electrode was then taken up in a 50-50 mixture of concentrated nitric and sulphuric acids, and

[3]An ammonium acetate - acetic acid buffer of the same pH seems to inhibit the solution of both the copper and the zinc.

the surface of the electrode was rinsed with distilled water. In the early experiments, the resulting solution was dilute enough to require concentration by boiling. In the later experiments less acid and less rinse water were used so that concentration was not necessary.

The above procedure was repeated, cutting through the bakelite lacquer over the body of the crystals instead of over the grain boundaries. These cuts were made close to, and roughly parallel to, the grain boundaries in order to minimize any errors due to any possible failure to attain complete homogeneity inside the body of the

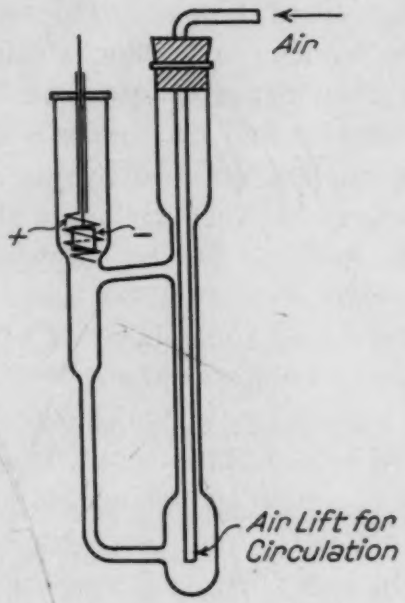

Fig. 2—Micro-electrolytic Cell.

crystals. The total length of these cuts for a given run was substantially the same as those made in the grain boundaries. In this way, equal quantities of etched-out material represented etching-grooves of substantially the same depth. It should be noted that our spectrographic analysis from these cuts near the boundaries of the crystals agreed within the precision of the measurement with the over-all wet analysis of the specimen, thus tending to confirm our previous conclusion that our time of anneal at 410 degrees Cent. (770 degrees Fahr.) was sufficient for our purpose.

In order to make sure that this technique gave analytical results free from any preferential solution of zinc in the electrolytic etch, the following experiment was tried: A specimen whose copper con-

tent was known to be 1.70 ± 0.2 per cent by ordinary wet analysis was coated with bakelite lacquer, and cuts were made in the lacquer without any reference to grain boundaries. An electrolytic etch was made in these cuts at a voltage of 10 volts, and a current of 2 milliamperes. The amount of sample removed in this way was about 10 milligrams. Using the spectroscopic technique described below, the spectrum of this sample was photographed. A piece of the original specimen was wholly dissolved in a 50-50 mixture of sulphuric acid and nitric acid. A portion of this was taken containing 10 milligrams of metal and its spectrum was photographed adjacent to that of the electrolyzed sample. The two spectra were indistinguishable. Since, as described below, a difference of 0.1 per cent in the composition of standard samples can be detected, it was assumed that all the zinc and all the copper had been removed simultaneously from the surface exposed by the stylus. The fact that such a good check was obtained makes it also possible to assume either (a) that the zinc and the copper which had been removed from the specimen were completely recovered on the platinum electrode, or (b) that the zinc and copper were recovered in the same ratio in which they had existed in the electrolyte during ionic transfer to the platinum electrode. The voltage used on this test was the minimum used in subsequent etchings. It was, therefore, assumed that there was no preferential etching out of zinc from the cuts along the grain boundaries. The spectrograph was a 3-prism quartz instrument of high dispersion and resolution designed and constructed by the writers.

In the subsequent quantitative spectrographic analysis, graphite rods, containing the materials to be investigated, were used. These graphite rods 12 inches by $\frac{5}{16}$ inch were obtained from the Bausch and Lomb Optical Co. and were in a high state of purity. The only impurities that were found in considerable amounts were silicon, phosphorus and magnesium. For practically all spectrographic work these electrodes are highly satisfactory. Two-inch lengths were cut and the ends cut to a blunt chisel shape. The electrode which was to be the positive terminal of the arc was drilled to a depth of $\frac{1}{8}$ inch and a diameter of about $\frac{1}{8}$ inch. The carbons were fixed in a special arc holder and burned for a short time with a direct current of about 6 amperes. This insured sufficient porosity so that the positive carbon could absorb the amounts of material to be analyzed. The material to be analyzed was placed in solution form in the hole

in the positive electrode. This carbon was dried for one hour in an oven at 115 degrees Cent. and was then placed in the arc holder with its chisel edge parallel to the axis of the collimator. With a separation of approximately 2 millimeters between the chisel edges of the carbons, an arc was struck between the two electrodes by means of a pure carbon rod. A quartz condensing lens focused the arc on the slit of the spectrograph. Exposures of 1-minute duration were found sufficient to completely volatilize 1 milligram of material. It was necessary to decrease the aperture of the condensing lens by a diaphragm because at full aperture the 1-minute exposure was sufficiently long to bring out the background spectrum of carbon.

A series of standard solutions containing varying proportions of copper in zinc was prepared. The spectrographic analysis consisted of exposing, adjacent to one another, spectra in the following order:

(1) Grain boundary sample
(2) Grain interior sample
(3) Standard solution (A)
(4) Standard solution (B)
(-) ..... (-)
(m) Standard solution (N)

For quantitative spectrographic analysis the ultimate or persistent lines are not suitable for the range such as used in this investigation. Spectral lines of less persistence show within certain ranges rapid changes of intensity with changes of concentration of analyzed substances. For copper the line at 2618.39 Å was found best suited for analysis. At 2 per cent the line is quite strong and at 0.5 per cent it disappears almost completely. Unfortunately this sensitivity requires a total copper content of at least one microgram. For comparison with the known standards the zinc line at 2670.57 Å was used as the second member in the homologous line pair method (7), (8), (9). This method makes use of the ratio of intensity of the unknown line to a weak line due to the major constituents. Thus any external variations such as slight fluctuations in the exciting current or tendency of the arc to wander from the slit will affect the intensity of both lines in the same manner but not their ratio. The only errors that would be produced would be due to variations in volatility and excitation of the copper and zinc atoms.

Experimental Results

The following specimens were investigated:

Specimen	Copper Content by Wet Analysis of Massive Sample	Remarks
3a	1.07	
3b	1.07	3a re-ground and polished
6a	2.07	
6b	2.07	other half of 6a
7a	1.65	
7b	1.65	other half of 7a

Specimen 3a. Spectrographic analysis of material from the body of the crystal showed a Cu content of 1.1 per cent. In getting the sample of grain-boundary material, the solution of sample was made too dilute, so that the spectrum lines were very weak, but still usable. The copper content at the grain boundary was determined to be 0.8 per cent.

Specimen 3b. This was a second specimen obtained from the same ingot as 3a. The copper content of the body of the crystals was again 1.1 per cent. The sample of material from the grain boundaries was more concentrated than in the case of 3a. The copper content of the grain boundaries was 0.7 per cent.

Specimen 6a. The copper content was found to be 2.1 per cent in the body of the crystals, and 1.6 per cent at the grain boundaries.

Specimen 6b. This specimen was taken from the other half of the ingot used for 6a. The copper content was found to be 2.1 per cent in the body of the crystals and 1.8 per cent at the grain boundaries.

Specimen 7a. The copper content was found to be 1.6 per cent in the body of the crystals and 1.5 per cent at the grain boundaries.

Specimen 7b. This specimen was taken from the other half of the ingot used for 7a. The copper content was found to be 1.6 per cent in the body of the crystals and 1.4 per cent at the grain boundaries.

In all the above, the match of intensity of line between spectra of the unknown and spectra of the standard was good enough to detect the difference between, say, 0.7 and 0.8 per cent copper, or between, say, 1.4 and 1.5 per cent copper. Microphotometric measurements were also made on the spectrum plates. No increase in precision was obtained but the visual estimations were thus substantiated in every case.

Discussion of Results

The differences in composition found above are so striking and so large in comparison with the errors of measurement that it is hard to escape the conclusion that the concentration of a solid solution is different at the grain boundaries from that in the body of the crystals. In view of the close approach to equilibrium indicated at the beginning of this article, it would seem reasonable to interpret our data in the light of the Gibbs isotherm. From this point of view, the decrease in copper content at the grain boundary would mean that copper tends to raise the interfacial tension between crystalline zinc and the disorganized semi-crystalline grain-boundary material. This would be likely to happen (10) if the surface tension of copper were higher than the surface tension of zinc. Data quoted in the 1936 edition of the A.S.M. Metals Handbook (11) indicate that at 450 degrees Cent., (840 degrees Fahr.), (which is only 40 degrees above our annealing temperature), the surface tension of zinc is about 755 dynes per centimeter and that of copper at 1140 degrees Cent. (2085 degrees Fahr.) is about 1120 dynes per centimeter. If these values can be used to indicate anything about the surface tensions in the solid state at 410 degrees Cent. (770 degrees Fahr.), we may have some little justification for our application of the Gibbs isotherm. Such a line of reasoning would indicate an excess concentration of zinc at the crystal boundaries of a solid solution of zinc in copper (alpha phase). It would be interesting to repeat the present work at that end of the copper-zinc constitution diagram to see if such a prediction could be verified.

Summary

(1) A technique has been developed for obtaining, in a form suitable for spectrographic chemical analysis, specimens of material representing primarily crystal-boundary material which may be compared with other specimens of material from the body of the crystals themselves. Specialized equipment, developed for this purpose, has been shown by means of diagrams.

(2) By spectrographic chemical analysis it has been shown that the concentration of solute in a solid solution is different at the intercrystalline boundaries than it is in the body of the crystals.

(3) It has been shown specifically that copper is more soluble

in the body of the crystals of solid solutions of copper in zinc than in the intercrystalline boundaries of those same solid solutions.

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DISCUSSION

Written Discussion: By E. A. Anderson and J. L. Rodda, N. J. Zinc Co., Palmerton, Pa.

It has long been suspected, and indeed the probability was pointed out in a paper from this laboratory appearing as Technical Publication 174 of the Institute of Metals Division of the A. I. M. E., that the solubility of one metal in another was different in the grains and the grain boundaries. The present authors are to be complimented on their efforts in securing actual experimental verification of this hypothesis. They are further to be complimented on the use of the spectrograph in the conduct of their quantitative analyses. No other means permits the accurate determination of the elements present with such small amounts of sample.

We wonder whether the authors had considered what appears to us to be, potentially at least, a more sensitive method for analyzing grain boundary material. This method consists of fracturing the specimen under conditions usually of high temperature which forces the fracture to take place in the grain boundaries. By exciting the spectra by spark methods between the fractured surfaces as electrodes, it should be possible to obtain a very delicate measure of the composition of the grain boundary material. Selective etching under controlled conditions should permit measurements of composition to be made at various depths in the grain from the boundary.

The one criticism which we might make of the work is that while there is considerable evidence that the annealing time was actually sufficiently long to permit complete equilibrium to be reached, the writer's experience with this

type of alloy would lead him to believe that there was still some chance that a small deviation from true equilibrium might still have existed. This comment has no bearing on the authors' findings with regard to the actual existence of a difference in composition between the grain and the grain boundary but may have some bearing when the exact quantitative difference is inspected.

Oral Discussion

L. L. WYMAN:[1] If we take into consideration the fact that there may be a variation in the concentration of the solvent solid solution between the interior of the grain and the boundary itself, I wonder if it would not be interesting if we took a sample and did something to it which violates one of the well known laws of grain growth, and move that boundary a little bit and repeat the experiment to see whether or not the change in concentration moves with the boundary.

W. P. DAVEY: The difficulty in that is inherent in the nature of the material. There is a phase change which is tied up with a definite temperature which has to be taken into account. It was necessary to heat each of these materials and then quench it in order to maintain the solubility at a big enough value and still have the zinc structure in the individual grains. We ran into a great deal of trouble until we learned just where that boundary line in the phase diagram was; since the published phase diagrams for metals are more or less schematic, the whole story had necessarily to do with the difference in solubility in the solid solution state and in the intermetallic compound state.

L. L. WYMAN: I realize that in this particular case you are concerned with that problem, but, as applied to the general case, if we were dealing with a material in which no transformation was involved at all, which, to the best of our knowledge, is a complete solid solution system, there would be range enough so that we could cause a little recrystallization, only move that boundary over there a very minute amount, and repeatedly experiment. It would be very interesting to see what happens in the old position as compared with a new situation of the boundary.

W. P. DAVEY: That would be very interesting in the general case but it could not be applied in this case.

In connection with the written discussion, we looked up the literature on zinc-copper diagrams and especially the Hansen and Stenzel constitution diagram for copper-zinc, which apparently is the best one now known. We then heated our specimens twice as long as the literature indicates is necessary for equilibrium. I think that Anderson and Rodda's objection to the length of time of our anneal is hardly valid. They would like to see us anneal for about five times that long, because at other portions of the constitution diagram, where the proportion of copper is higher, the time of heating must be longer than that used by Hansen and Stenzel. For the copper range we had, we think we heated for a sufficiently long time. The reason we think so is that we got the same analysis from a scratch made parallel with the grain boundaries that we got from other scratches made at random, (the two scratches being of approximately the same total over-all length). As far as we know all conditions were identical.

[1]Research metallurgist, General Electric Co., Schenectady, N. Y.

We got the same spectrographic analysis next to the grain boundaries that we did by ordinary wet methods for the body of the crystal. We have also made other spectrographic analyses in which we compared a scratch made near the boundary of the crystal with other scratches made further inside the crystal. Again we got the same analysis showing that the constitution inside the crystal was practically uniform. As to the heating of the crystal and hitting it with a hammer and trying to make it fall apart because of the weakening of the intercrystalline bond: we considered that and tried it a little bit, but it did not seem to be as good a technique as the one reported in our paper. We worked on the spectrograph so as to use a spark as well as an arc, but we were afraid to use the spark on the surfaces of the individual crystals because there was no assurance that we could determine accurately when to quit sparking. If one continues sparking indefinitely, one gets into the body of the crystal and then the analysis is misleading. We thought it was much safer to use the technique outlined in our paper.

A NOTE ON RAPID PHOTOMICROGRAPHY

By Willard Mutchler and Henry O. Willier

Abstract

A rapid and relatively inexpensive method for making photomicrographs on a metallographic microscope is described. An apparatus, designed to hold roll film or paper, is substituted for the individually loaded film-holders used in ordinary practice. The use of an auxiliary focusing eyepiece makes it unnecessary to remove the holder when focusing, since the image is duplicated upon the independent eyepiece.

Bromide emulsion photographic papers, of appropriate thinness, may be used for quantity work. The image obtained on the paper negative shows sufficient detail for many purposes, and may eliminate the need for prints. Prints of good quality can be made, however, from the paper negatives.

At times, in both metallurgical research and industrial practice, it is necessary to examine large numbers of specimens on the metallographic microscope. Under such circumstances, even though a complete pictorial record may be distinctly advantageous, photography is usually reduced to a minimum because of the time and cost requirements. It is the purpose of the present paper to outline a rapid and inexpensive method for obtaining photomicrographs, which is now being used successfully at the National Bureau of Standards.

Most metallographic microscopes are ill-adapted to photomicrography on a quantity basis, if rapidity is an important factor. The proper focus for each area selected must be determined on a ground glass at the end of the camera bellows; and plate or film holders individually loaded and later substituted for the ground glass. Frequently, one man's entire time is delegated to loading and developing, while another, stationed at the microscope, takes the photographs.

Published with the approval of The Director of the National Bureau of Standards of the United States Department of Commerce.

A paper presented before the Nineteenth Annual Convention of the Society held in Atlantic City, October 18 to 22, 1937. Of the authors, Willard Mutchler is Assistant Metallurgist and Henry O. Willier is Junior Physical Science Aid, National Bureau of Standards, Washington, D. C. Manuscript received June 25, 1937.

In order to reduce time greatly in loading and unloading, a roll holder of simple design was constructed which permits the use of paper or film. A view of the holder, in position for operation, is shown in Fig. 1. The roll is loaded into compartment A, the paper threaded through the exposure plane, and the end attached to a spool

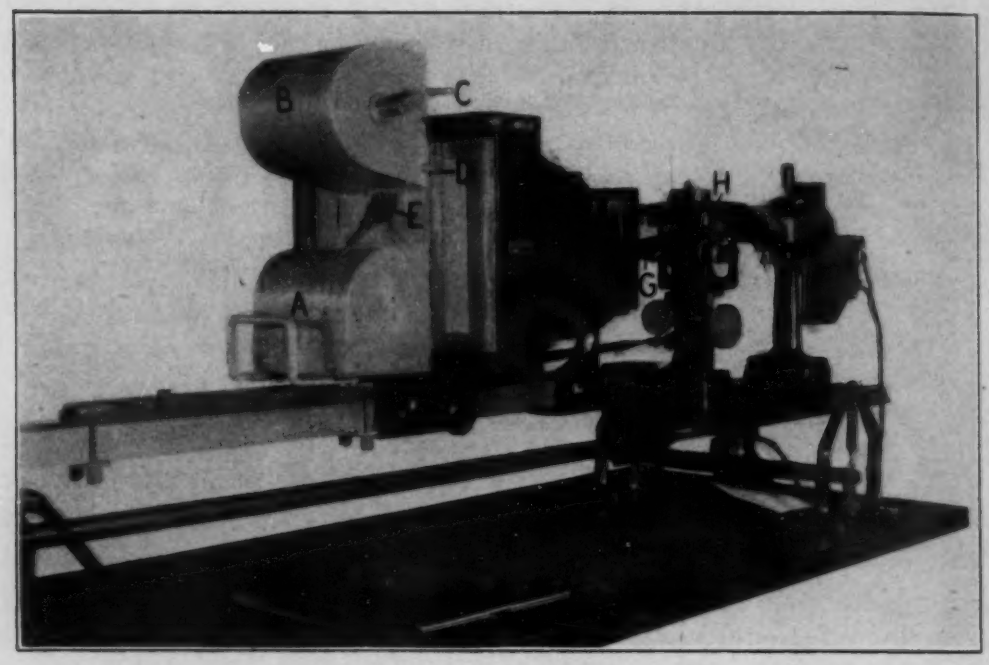

Fig. 1—View of Holder, Containing Roll of Film or Paper, in Position for Operation. The Paper is Moved from Compartment A to B, by Crank C. Pointer D Makes One Revolution When the Paper Has Moved the Length of the Exposed Negative. E is an Autographing Device. The Holder Rests on the Track F. A Split-beam Prism at G Reflects Part of the Light to the Eyepiece H. $\frac{1}{10}$ Natural Size.

in compartment B, rotated by means of the crank C. The crank moves the exposed area out of the exposure plane, putting a new area in position for the next exposure. The pointer D, attached to a measuring roller, indicates the movement of the paper. A pencil at E, mounted in a light-tight flexible hood, is used to autograph identification symbols on the back of the paper. The entire holder is supported by an inverted tee-unit which fits into the adjustable track, F, so that both the holder and track may be removed when desired.

A split-beam prism, mounted at position G, reflects part of the light to the auxiliary eyepiece H. These units are so arranged that both the field of view and the focus, as seen at the eyepiece, are identical to those impinging on the film. These auxiliary focusing eyepieces are standard equipment with some types of photomicro-

graphic apparatus. Their use results in a very appreciable saving in time, since the holder need not be removed until the entire roll has been exposed.

A view of the interior of the holder, which reveals its construction in more detail, is shown in Fig. 2. The covers, A, and the sides, B, are removable for loading purposes, being attached by means of bolts and thumb-nuts. The inner edges of the covers are lined with black felt which assures light-tightness. The film is mounted on spools which rest on the supports, C. The engaging shaft G, of the crank, fits into a slotted end of the spool, to effect its rotation. The paper or film passes between the cover-plate, D, and the front-plate, E, and emerges under the rubber-covered measuring cylinder, F, the circumference of which equals the length of the exposed area.

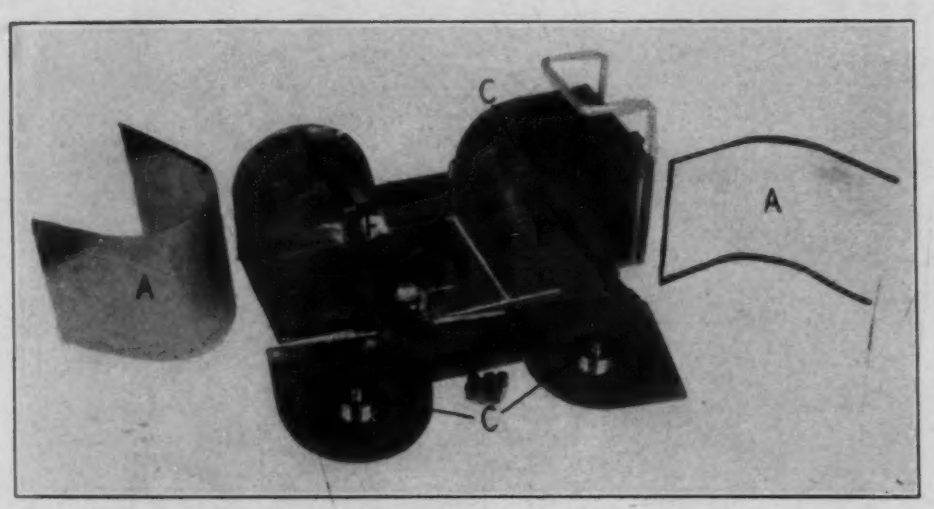

Fig. 2—View of Interior Details of Construction Showing A, Top Covers; B, Sides; C, Spool Supports; D, Cover-plate; E, Front-plate; F, Measuring Cylinder; G, Engaging Mechanism of the Crank. The Paper or Film Leaves a Spool on the Right, Passes Between Plates D and E, Emerges Beneath the Cylinder F, to be Fastened on a Spool at the Left. $\frac{1}{10}$ Natural Size.

The spools, shown in Fig. 3A, are of the usual design. A 4 x 5 inch aperture in the front-plate, as seen in Fig. 3B, limits the exposure area. Fig. 3C illustrates the assembled holder, with only the top covers removed. The handle at the left of Fig. 3C is used to move the holder when mounted on its track support.

The holder was designed for negatives 4 x 5 inches, but provision could readily be made for any size up to 8 x 10 inches. With alterations, the apparatus can be adapted to permit the exposure and development of one or more photomicrographs in a manner similar to that used in photostat machines. The paper or film, for example,

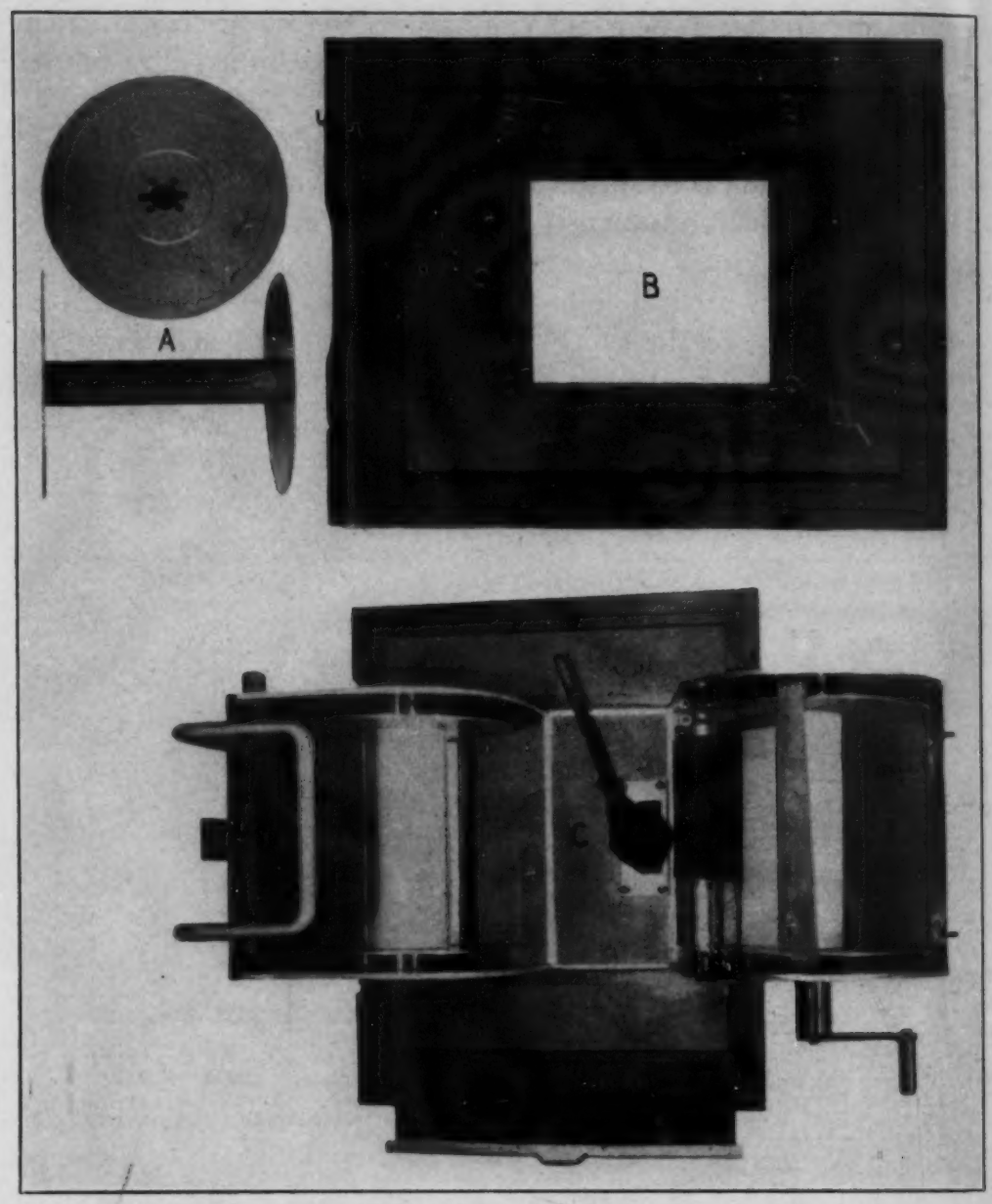

Fig. 3—View Showing Additional Details of Construction; A, the Spools; B, 4 x 5 Inch Opening in the Front-plate; and C, the Assembly with the Top Covers Removed. Approximately ⅛ Natural Size.

could be conveyed into an easily removable compartment, and severed by a suitable shearing mechanism.

It is evident that the apparatus, especially if used in conjunction with a split-beam prism focusing eyepiece, effects a major saving in time. Appreciable savings in cost can be made by using appropriate papers, instead of film, for negative material. Bromide emulsion papers, of the standard photostat grades have been found suitable,

Fig. 4—Appearance of Images Obtained on Paper Negatives, Showing the Extent of Corrosion in Two Aluminum Alloy Sheets Corroded by the Salt Spray Method in 20 Per Cent Sodium Chloride Spray. Sheet A, Alloy 52S, is Practically Unattacked After 9 Months' Exposure. Sheet B, Improperly Heat-treated 17S (Duralumin), Exhibits Severe Intercrystalline Attack After 6 Months' Exposure. The Two Sheets Were Originally of the Same Thickness as Shown by the Arrows. Reduced from × 50 to × 25.

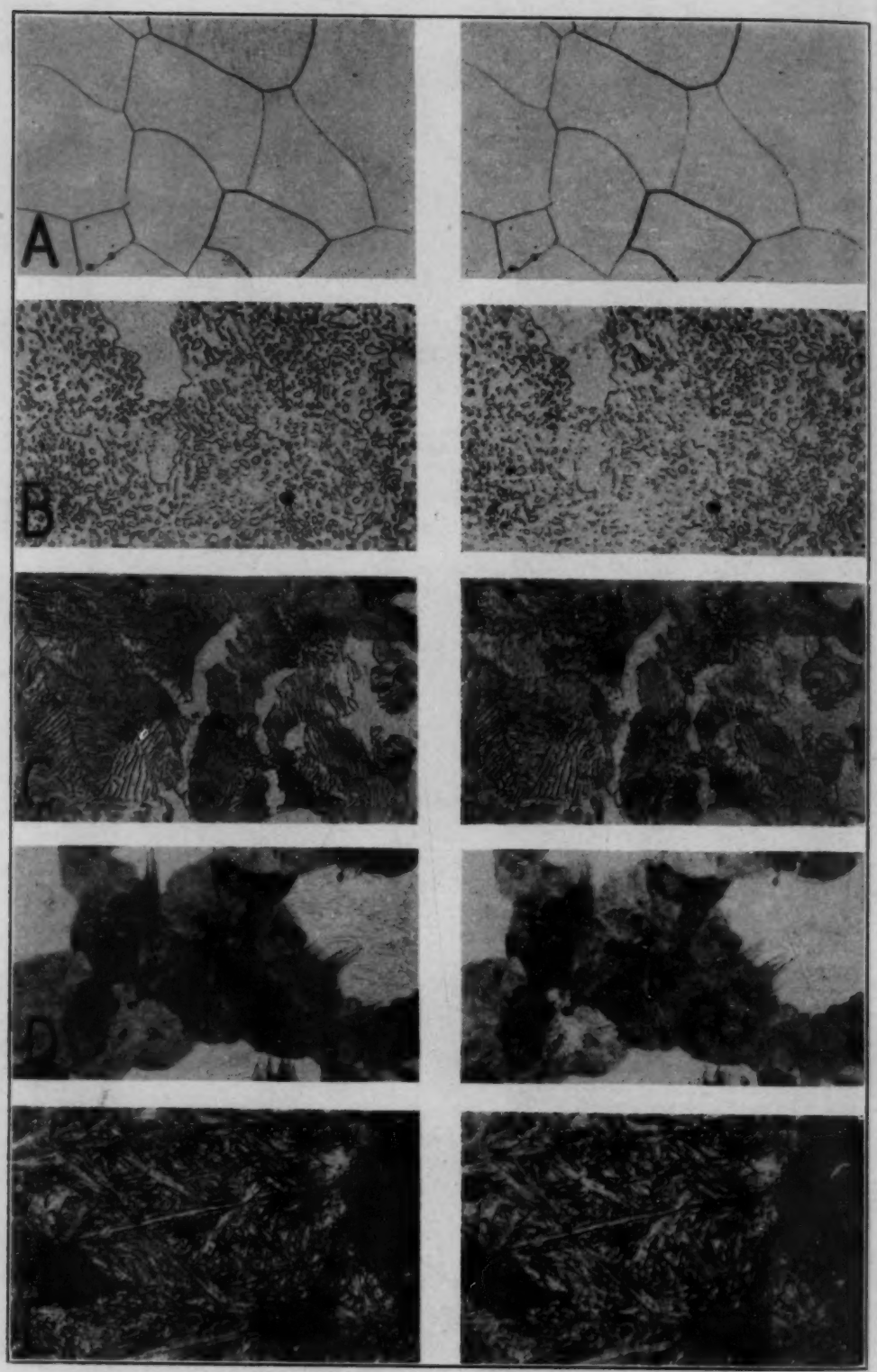

Fig. 5—Shows the Comparative Quality of Prints Made from Orthochromatic Films (Left) and from Paper Negatives (Right). The Areas Pictured Are the Same in Each Instance. A, Ferrite; B, Spheroidized Cementite; C, Pearlite; D and E, Martensite and Troostite. A is × 100; the Others, × 500.

and can be obtained in rolls up to 350 feet in length, and in appropriate widths on special order. The holder, as designed, is loaded with a roll of "22-substance" paper 5 inches wide, which permits some 900 exposures from one loading. The individually autographed exposures are cut off the roll in a dark room, developed, fixed, washed, and dried after the fashion of prints. It should be mentioned that the use of paper negatives and roll paper holders is quite old. Daylight loading roll paper negative holders were patented as early as 1854.

The corrosion behavior of some 7000 specimens of aluminum alloy sheet materials, 9 x 0.75 x 0.064 inches, is being currently investigated at the National Bureau of Standards. These specimens are exposed to corrosive conditions and groups are removed periodically for further tests in the laboratory. An important item consists in examining under the microscope four random cross sectional areas, each 0.5 x 0.064 inch, from every specimen. The appearance of each area, at 50 diameters, is photographed on paper negatives, thus furnishing permanent records of the type shown in Fig. 4. Six separate exposures are necessary to make a complete picture of each 0.5x 0.064 inch cross section, and upwards of 700 negatives can be made in an average working day. It is readily apparent that the accomplishment of this task by the commonly practiced methods of micrography would be prohibitive.

The image on the paper negative reveals sufficient detail to obviate the need for making prints. The rate of progress of corrosion can be seen at a glance by laying out the negatives in chronological order. If desired, the depth or area of the corroded portions may be readily measured on the negative.

Prints may be made from the paper negatives, although the quality is usually somewhat inferior to those made from film negatives. The prints, however, possess sufficient detail for most routine examinations. The differences in quality are exemplified in Fig. 5, which shows typical microstructures of identical areas with prints made, in one instance from orthochromatic films, and in the other from paper negatives.

This method of photomicrography has proved to be rapid and satisfactory and with paper negatives, relatively inexpensive. It is believed that this apparatus or modifications of the same may find use in other applications of micrography and photography.

DISCUSSION

Written Discussion: By E. H. Dix, Jr., Research Laboratories, Aluminum Co. of America, New Kensington, Pa.

The writer has been favored by seeing this equipment in operation and in observing a great many of the results obtained. In his opinion it accomplishes everything that the authors claim for it.

The value of a rapid and inexpensive method for obtaining records of large areas of the surface examined certainly will greatly aid in the more general use of a photographic record. This is highly desirable because too often the results of microscopic examination depend almost entirely upon the interpretation placed upon the structures found, by one observer with perhaps one or two photomicrographs to illustrate the description given by the observer. With this new method a number of people will have an opportunity to see the evidence and draw their own conclusions.

Messrs. Mutchler and Willier are to be complimented upon the development of this new rapid method and they deserve the thanks of all of us for describing their equipment and procedure in this paper.

Written Discussion: By H. W. Zieler, E. Leitz, Inc., New York City.

It was only natural that the writer, when perusing the paper by Messrs. Mutchler and Willier, tried to find ways or means to use commercially produced equipment for the same purpose. And it was only natural that, in this search, the miniature camera with equipment for photomicrography loomed up. Those familiar with equipment belonging to the miniature camera may know that there is a special adapter available for photomicrography consisting of a regular microscope eyepiece mounted to a mechanism which contains a beam splitting prism, a side viewing telescope, a shutter, and an intermediate adapter ring for adaptation to the miniature camera body. There are also special models of these miniature camera bodies which hold sufficient standard 35mm motion picture film for 250 exposures.

In making comparisons between the method of using this miniature camera equipment and the specially built paper holder described in the above paper, and in weighing the advantages and disadvantages of both methods, the following conclusions were arrived at:

The method involving the paper drum has some very attractive features such as the possibility of making notes on the back of the paper for each negative frame. There is also the advantage of severing individual negatives for separate development. On the other hand, it seems that the use of sensitive papers has certain disadvantages. In the first place, even the finest bromide papers are not as light-sensitive as many photographic plates and films. The papers are generally not orthochromatic or panchromatic, and their range of sensitiveness will hardly allow the use of green filters. If the focusing is done without any filter at all, it does not seem very certain for photomicrography.

The use of a miniature camera with standard 35mm motion picture film has a few additional attractive features. Film emulsions are available in a great range of sensitivity. Even panchromatic films for direct reversal are available so that the picture taken with the photomicrographic equipment comes out directly as a positive on the film and can be used for projection purposes.

The rendition of detail on the small negative films, as practice has shown, leaves nothing to be desired and the projected image from one of these small negatives will certainly show more detail and a better quality of the picture than copies made from paper negatives. The standard motion picture film requires a much shorter exposure not only because it is more sensitive than photographic papers but also because of the small negative size. Under almost any condition it will be possible to take instantaneous photographs.

The question of film storage also seems to offer advantages. A single roll of one hundred feet of motion picture film contains eight hundred negative frames 24 x 36mm and a roll of this type naturally takes much less space than a paper roll with negatives 4 x 5 inches containing eight hundred negatives. The miniature camera equipment also has a side telescope and inasmuch as the distance from the eyepiece to the film is constant, there is no necessity of making corrections with the side telescope which must be made when this focusing eyepiece with beam splitting prism is used on a camera with variable bellows. A further increase of the light intensity in the plane of the film, when using the miniature camera equipment, can be obtained by swinging out the beam splitting prism.

To summarize, the method with the miniature camera has great advantages. It has been used successfully in metallography particularly in one instance. If a heating stage is placed on the object stage of the microscope, and if changes of the structures of the specimen which occur during the process of heating have to be recorded photographically, the speed and convenience of taking pictures with the miniature camera is a great help.

The disadvantage of this method seems to be that we do not have the possibility of making notes on each negative frame. On the other hand, it is possible, though not quite convenient, to cut off certain lengths of the film and develop them separately.

Written Discussion: By A. W. Winston, The Dow Chemical Co., Midland, Mich.

In describing their apparatus for rapid photomicrography using roll film or paper, the authors have presented us with a method of considerable value in many applications. For routine records on a production scale, as in the corrosion studies which are cited in the paper, the saving in time and material cost is obvious compared to the usual method of single film exposures.

The research worker with a dozen or two negatives to be taken each day probably would find the equipment clumsy and inconvenient for his needs, particularly if it is desired to develop individual exposures as they are made. The slight loss of definition might be important to him, although it would not seem to be significant for ordinary work. The use of the split beam prism is necessary with the fixed film holder. It is the present writer's experience that direct focusing on the ground glass which carries an outline showing the position of the film allows one to move the field so that the best placement of the image on the film is made. Such maneuvering of the field at magnifications of X100 or over is difficult unless one watches the image on the ground glass while the change is made.

The effect of the use of bromide paper upon the exposure time is not

discussed in the paper. It is generally known that the exposure required for bromide or photostat paper is approximately ten times that for panchromatic film. With arc illumination, this factor may not be significant, but with tungsten bulb illumination, the actual increase in time may be much more than the time to load a separate film holder. This would be more noticeable as the contrast of the bromide paper is increased.

During the last few weeks, the writer has been connected with an attempt to develop an economical and rapid photographic method for recording molding methods for sand castings. The present plan is to use direct positive paper in individual film holders with a reversing prism in front of the camera lens. This paper does not possess the latitude of film and, as the positive image is obtained by reversal, exposure errors cannot be compensated for in printing. However, when the illumination can be standardized, satisfactory results are obtained. As the stock is waterproofed and fixing is not required, positive prints can be delivered dry, ready for mounting, within five minutes after exposure. Additional prints must be made by copying rather than by contact or projection printing.

Limited attempts have been made recently to use this direct positive paper for photomicrography. The resulting prints, while exhibiting sufficient detail, were muddy in appearance and lacked contrast. This may have been due to errors in exposure or development and reversal, but probably was due to the softness of the emulsion. If a contrast grade of direct positive paper were available, it could be used for single exposures or in the equipment designed by the authors with further saving in time to produce positive prints.

Authors' Closure

The authors greatly appreciate the discussions submitted by Messrs. Dix, Zieler, and Winston. They concur with Mr. Zieler's suggestion that commercially available miniature camera equipment might well be used advantageously on metallographic microscopes. Such equipment would form an ideal means for photography in certain instances where a large quantity of records are desired. The use cited in connection with structural changes in metals undergoing heating is both pertinent and interesting.

However, it is believed that a roll holder of the type which we have described could be produced and marketed at much less cost than a miniature camera and its accessories, and yet prove equally satisfactory for many purposes. Furthermore, the negatives would be of correct size and magnification without recourse to projection or enlargement operations.

It was not intended to convey that the use of bromide papers would yield results as excellent as those obtainable upon films. The photographs in Fig. 5 merely exemplify that paper negatives may be satisfactory. A K2 filter was used in conjunction with the bromide papers and the exposure times ranged from 2 to 20 seconds, depending upon the brightness of the surface photographed. The exposures on the orthochromatic, under identical conditions and with arc illumination, seldom differed by more than 3 seconds from the time required for the paper.